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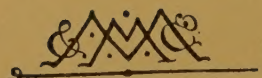

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A MANUAL OF PRACTICAL PHYSICAL CHEMISTRY

BY

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TO

PROFESSOR F. R. JAPP, F.R.S.

PREFACE

In organising the practical work in connection with a class of Physical Chemistry (1) a teacher may himself carry out the measurements while the whole class look on, or (2) he may divide the class into sets of two or more and assign one experiment to each set, or (3) he may adopt the "one student one experiment" plan. Of these three methods, the third is undoubtedly the best, because a student is made responsible for an experiment in a way that can never be when another is associated with him in the work. In the second method the tendency is for one student of a set to lead while the others make no attempt at initiative and lose the best part of the training obtainable in a laboratory. Close supervision is, of course, essential when valuable instruments are being handled, and frequently the teaching staff is too small for the demonstrating to be efficient according to the third plan, so that the second is adopted, which, however, is much to be preferred to the first.

The time available for Practical Physical Chemistry is usually very meagre, and has an important bearing on the organisation of Laboratory Work. The best system would be one in which the question of time had never to be considered. As things are, however, a student, as a rule, can afford out of his day's work only one period of two to three hours for Practical Physical Chemistry. It is important, therefore, that the exercises should be such that they can be finished in one period not extending beyond the limits mentioned. This

restriction of every exercise to a time-limit greatly assists a teacher in organising the work of large classes in which all the students are working during the same period though not at the same exercises, and in which it is important that no experiment should require to be carried over from one period to another, otherwise the class-work would be disorganised.

I have had occasion to devise a series of such time-limit exercises, and the present book has grown round instruction-sheets written by me in connection with laboratory work here. This manual contains a series of 39 time-limit exercises, which are numbered to facilitate organisation. I have also written introductions to some sections of the subject, and in these parts of the book and elsewhere will be found several important experiments which are not numbered and which will form suitable exercises when unlimited time is available. Thus an endeavour has been made to meet the needs of all classes of students.

In the selection of the experiments, there has been constantly kept in view their value as illustrating theory and their importance on account of applications to other sections of chemistry and to other sciences. Even with the restriction as regards time it may be claimed for the exercises that they are highly instructive and cover a wide field of the subject.

With regard to the time-limit exercises, it should be noted that in some cases the apparatus must be fitted up by the demonstrator beforehand, or kept fitted up throughout the course. It would be impossible otherwise to organise an evening course, for example.

In this work I have paid special attention to the subject of accuracy, which is discussed in the introduction. The treatment of this subject in books on Physics and Physical Chemistry, both theoretical and practical, is inadequate and in most cases unsound. Considerable confusion has arisen, for example, in connection with the term "probable error" and in the use of the sign $\pm$ in the theory of errors.

Several parts of this book, both in the text and in the diagrams, are not to be found in any text-book on Physical Chemistry. All the diagrams have been specially drawn for this work. The methods described are up-to-date. The text is made as concise as possible, consistent with clearness; a full discussion of theory is, of course, precluded in a book of this scope.

It is impossible to acknowledge all the books on Physics and Chemistry which have assisted in connection with the present work, but mention may be made of Ostwald-Luther's *Physiko-chemische Messungen*, which would form a suitable text-book for more advanced study. I am also very pleased to recommend Kaye and Laby's *Tables of Physical and Chemical Constants*, which is constructed on sound principles, and should be in the hands of every student of Physical Chemistry. I must also express my indebtedness to the excellent Landolt-Börnstein *Tabellen*.

I am glad to acknowledge the permission I obtained to reprint the tables of logarithms and antilogarithms, which are from Frank Castle's *Logarithmic and Other Tables* (Macmillan and Co.).

The present volume is the result of several years' experience in the teaching of Physical Chemistry, and it is hoped that what has proved helpful to the author will find a more extended sphere of usefulness both in day and in evening classes.

F. W. G.

Aberdeen University, 1914.

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PRACTICAL PHYSICAL CHEMISTRY

ACCURACY.

In making a series of measurements of the same quantity, different values are obtained. The nearer these values are to one another the less is the **error of observation**, or in other words the greater is the **precision** or **sharpness** of the result. The error of observation or fortuitous error is the most persistent of all errors, and no experiment is ever free from it. Due to this error any individual value obtained is as likely to be greater than the correct value as less. The **arithmetical mean** of the values is likely to be nearer the correct value than is any single value of the series. The arithmetical mean is the most likely value of the quantity so far as we can judge from the data.

The difference between one of the readings obtained and the arithmetical mean is called the error of that reading, and the arithmetical mean of the differences (the signs being ignored) may be called the **average error** of a reading.

If one reading differs considerably from the others, we are not entitled for that reason alone to reject it. The averaging tends to counteract the abnormality. However, we may have other good reasons for suspecting this reading, and its being widely different from the others would only serve to confirm this suspicion. For example, we may have noticed something erratic in the behaviour of the apparatus. In a case like this, we are quite justified in rejecting the value obtained. Methods sometimes are given for settling this question by means of a calculation.

The **error of observation** in a series of measurements may be small, and yet there may be involved in every case a **constant error** which affects all the values to the same extent and in the same direction, so that the result may be far from correct. Thus, **precision** and **correctness** do not necessarily occur together. In the meantime only errors of observation will be studied.

The following will illustrate the above remarks regarding errors of observation: A mass is weighed with the same balance at different times, and the following values are obtained:

Weights.	Deviations from Mean.
6·1241 grams.	− 0·00022 gram.
6·1244	+ 0·00008
6·1245	+ 0·00018
6·1241	− 0·00022
6·1245	+ 0·00018

Arithmetical Mean = 6·12432.

Mean (rounded off) = 6·1243.

Arithmetical Mean of Deviations = 0·000176
= 0·0002 (when rounded off).

Result is $6{\cdot}12432 \pm 0{\cdot}000176$,

or (rounded off) $6{\cdot}1243 \pm 0{\cdot}0002$.

The **average error** of one weighing is $\pm 0{\cdot}000176$.

It must be clearly understood that this refers to "error of observation" or "chance error" and not to "constant error."

In studying the error of observation we may consider either the **absolute error** or the **relative error**. In the above example the absolute error is $\pm 0{\cdot}0002$ gram and the relative error is $\pm \frac{0{\cdot}0002}{6{\cdot}1243}$, or approximately $\pm \frac{1}{30{,}000}$, or $\pm 0{\cdot}0033$ per cent.

Absolute error here does not mean the correct value of the error. *The correct value of the error is not known.*

The above result indicates that 6·12432 is the best estimate of the true value which the data will allow. The last two digits are uncertain and the 2 is used merely for rounding off

the other uncertain digit, which however we keep as 3, 6·1243 being nearer 6·12432 than is 6·1244.

The result also signifies that if we carry out one other measurement we may expect the weight obtained to lie within a certain range of weights with a probability which is expressed by the fraction $\frac{4}{7}$ approximately. The weights in this range do not differ from one another by more than $2 \times 0{\cdot}000176$, and extend from one which is greater than the correct weight by 0·000176 to one which is less than the correct weight by 0·000176. This means that if we repeated the measurement many times, *in the long run* four out of every seven values would be within the range mentioned. This fraction $\frac{4}{7}$ is the *probability* which can be shown to hold theoretically for a *range* the limits of which are indicated by the "**average error.**"

Other probabilities can be selected and the corresponding ranges measured. For example, $\frac{1}{2}$ *is the probability for the* "**probable error**" *range.* This means that the weight obtained in future weighings may be expected to be as often within the "probable error" range as outside this range. The so-called "**probable error**" therefore does not mean the *most probable error. The* "**probable error**" *means the limit to that range of errors the probability of which is* $\frac{1}{2}$.

Again, approximately $\frac{2}{3}$ is the probability for the range the limit of which is the "**mean error**" or the "**root mean square error**" or the **standard deviation.**

If d_1, d_2, d_3, ... d_n are the deviations from the mean and $\mathbf{a}$ = "**average error,**" $\mathbf{p}$ = "**probable error**" and $\mathbf{m}$ = "**mean error,**" then

$$\mathbf{a} = \pm\frac{d_1 + d_2 + d_3 + \ldots d_n}{n},$$

$$\mathbf{m} = \pm\sqrt{\frac{d_1^2 + d_2^2 + d_3^2 + \ldots + d_n^2}{n-1}},$$

$$\mathbf{p} = \pm 0{\cdot}6745\mathbf{m},$$

$$\mathbf{p} = \pm 0{\cdot}8454\mathbf{a},$$

or $\pm 1{\cdot}18\mathbf{p} = \mathbf{a}$;

also $\mathbf{m} = \pm 1{\cdot}253\mathbf{a}$.

In the above, n = the number of observations or readings. When n is large, $n - 1$ in the formula for **m** may be written n, and even if n is not very large we could substitute n for $n - 1$, provided we were certain that d_1, d_2, d_3, etc., are the correct values of the errors.

In dealing with different sets of measurements of the same quantity, or with sets of measurements of different quantities, *it is necessary to adopt the same method of range determination for the comparison of accuracy* and for the calculation of the accuracy of a result depending on two or more different quantities each of which is subject to error. The selection of **a** or of **p** as a standard is quite arbitrary, and the same may appear to be true of **m**, but this is not so; **m** is connected in an interesting and simple way with the theory of errors.

The fact that the probability of the **p**-*range* is exactly $\frac{1}{2}$ led to its selection as a standard, but the probabilities of the **a**-*range* and the **m**-*range* are not exactly $\frac{4}{7}$ and $\frac{2}{3}$, and do not explain why they are selected as standards rather than other ranges. The selection of the **a**-*range* is largely due to convenience in calculation. The **m**-*range* is wider than the other two and has a precise and simple relationship to the properties of errors, and its choice is less open to the charge of being arbitrary.

To obtain a clear idea of the properties of errors, suppose that we carry out a number of weighings of the same object, that the lowest weight obtained is 1·8977 grams and that we regard

Grams.		Grams.		Grams.
1·8977	and less than	1·8978	as equal to	1·89775
1·8978	„	1·8979	„	1·89785

and so on.

Further, suppose that we obtain the following:

1·89775	grams	25	times.	1·89825	grams	205	times.
1·89785	„	50	„	1·89835	„	170	„
1·89795	„	90	„	1·89845	„	90	„
1·89805	„	170	„	1·89855	„	50	„
1·89815	„	205	„	1·89865	„	25	„

At eleven points (in a straight line) on the paper at equal intervals from left to right, place the numbers

1·8977, 1·8978, 1·8979, 1·8980, 1·8981, 1·8982,
1·8983, 1·8984, 1·8985, 1·8986, 1·8987.

On the short lines between these points, erect rectangles whose areas are numerically equal to

25, 50, 90, 170, 205, 205, 170, 90, 50, 25.

The area of the first rectangle equals numerically the number of times the weight 1·89775 is obtained, or, in other words, the **frequency** of the value 1·89775. The area of the second

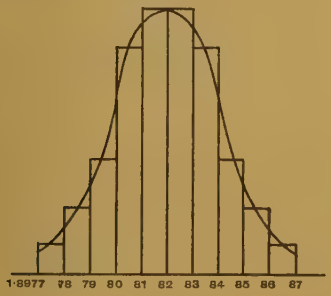

FIG. 1.

rectangle equals numerically the frequency of 1·89785, and so on for the other rectangles. The figure 1 shows all the rectangles, and the total area of the rectangles equals approximately the area subtended by the curve, or the area which equals numerically the whole number of observations. The breadth of each rectangle is largely a matter of choice, and if we choose it very small, then the total area of the rectangles is practically equal to the area of the curve.

It will be observed that the curve is symmetrical about a line, the part to the right of the line being the mirror image of the part to the left. The arithmetical mean of the weights, namely 1·8982, occurs at the line of symmetry. We expect to

obtain the mean at this position if we are encountering only chance or fortuitous errors.

Make the origin of our ordinates at 1·8982, then any point on the curve represents x and z, where x is a deviation from the mean and $z\,dx$ is the frequency of the deviation-range from x to $x+dx$.* If we are dealing with only chance or fortuitous errors, we should expect the frequency of positive errors to be as great as that of negative, and the symmetry of the curve is in accordance with this.

Instead of plotting the frequency F against the error x, it is often more convenient to plot $\frac{F}{n}$ against x, where n = the total number of observations. $\frac{F}{n}$ is the probability of the error x. For example, in the above, $n = 1080$ and, when $x = 0{\cdot}00045$, $F = 25$, and we should expect *in the long run* in future experiments to obtain, in 25 out of every 1080 observations, an error $-0{\cdot}00045$, that is, the probability of the error $-0{\cdot}00045$ is $\frac{25}{1080}$. Thus, by plotting in this way we obtain a **probability curve**. The curve is satisfied by the relation $y = \frac{h}{\sqrt{\pi}} e^{-h^2x^2}$, where $y\,dx$ = the probability of the error-range from x to $x+dx$ and **h** is a constant depending on the experimental method. The more precise the method the greater is **h**; in other words, the smaller is the deviation of all the values from the arithmetical mean, and the steeper the part of the curve next to the y-axis. If, in Fig. 2, the shaded area, which represents a probability, is extended along the whole curve, the probability becomes a certainty.

Note that the part of the curve nearest the y-axis is concave towards the origin, whilst the lower parts of the curve are convex. The points where a concave part passes into a convex are called **points of inflexion**. At the points of inflexion the

* dx here means the breadth of each rectangle in Fig. 1 when that breadth is very small.

values of the errors can be shown to be $+\mathbf{m}$ and $-\mathbf{m}$. Thus the range of errors from $+\mathbf{m}$ to $-\mathbf{m}$ has for its limits values corresponding to the points of inflexion on the probability curve; on the other hand, the points corresponding to **p** and **a** are on the concave part of the curve, and have no special characteristic distinguishing them from other points in the same

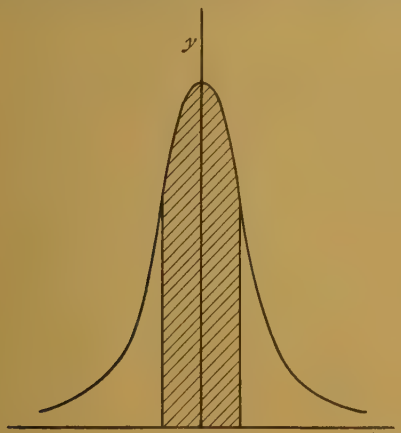

FIG. 2.

part of the curve. Moreover, the selection of the **m**-*range* for purposes of calculation brings this part of the subject into line with the rest of the theory of errors, which teaches that it is more correct to calculate with the squares of the range limits rather than with the range limits themselves.

Again, **m** bears to **h** (the characteristic constant for the method of observation under study) the simple relationship expressed by $\mathbf{m}^2\mathbf{h}^2 = \frac{1}{2}$. The more precise the method of measurement the greater is **h** and the smaller is **m**.

The probability of an observation having an error in the range from $+d$ to $-d$ is equal to the area subtended by the curve from $+d$ to $-d$ (see shaded part in Fig. 2). This area can be calculated by the Integral Calculus. Thus, for

the range from $+x$ to $-x$, the areas (or probabilities) have been calculated for various values of x, and published in the form of tables. What is usually given, however, in these tables is the value of the probability $\mathbf{P}$ (see Table I.), and the corresponding value of $\frac{x}{\mathbf{p}}$, where $\mathbf{p}$ is the "probable error," or the value of $\mathbf{P}$ and the corresponding value of $\mathbf{h}x$, where $\mathbf{h}$ is the constant of the probability equation $y = \frac{\mathbf{h}}{\sqrt{\pi}} e^{-\mathbf{h}^2x^2}$.

In the $\frac{x}{\mathbf{p}}$ table, for example, corresponding to $\mathbf{P} = 0{\cdot}5$, will be found $\frac{x}{\mathbf{p}} = 1$, *i.e.* for the range from $+x$ to $-x$ when $x = \mathbf{p}$, $\mathbf{P} = \frac{1}{2}$, and this, of course, is in accordance with the meaning of "probable error." Again, in the $\mathbf{h}x$ table, corresponding to $\mathbf{P} = 0{\cdot}5$, will be found $\mathbf{h}x = 0{\cdot}4769$; but $\mathbf{P} = 0{\cdot}5$ when $x = \mathbf{p}$, therefore $\mathbf{hp} = 0{\cdot}4769$.

We can show with the aid of the Integral Calculus that

$$\frac{\text{the sum of the squares of all the errors}}{\text{the total number of errors}},$$

or $$\frac{\Sigma(x^2)}{n} \quad \text{or} \quad \mathbf{m}^2 = \frac{1}{2\mathbf{h}^2},$$

or $$\mathbf{m}^2\mathbf{h}^2 = \tfrac{1}{2}.$$

But $\mathbf{ph} = 0{\cdot}4769$, therefore $\mathbf{p} = 0{\cdot}6745\mathbf{m}$,

$$\mathbf{m}^2 = \frac{\Sigma(x^2)}{n} \quad \text{or} \quad \frac{\Sigma(d^2)}{n-1},$$

where $x =$ a true unknown error

and $d =$ an error as actually found,

i.e. $$\mathbf{m}^2 = \frac{d_1{}^2 + d_2{}^2 + d_3{}^2 + \dots d_n{}^2}{n-1},$$

where d_1, d_2, d_3, $\dots d_n$ are the deviations from the mean.

Again, by using the Integral Calculus we can show that

$$\mathbf{a} \quad \text{or} \quad \frac{\Sigma(+d)}{n} \quad \text{or} \quad \frac{d_1 + d_2 + d_3 + \dots d_n}{n} = \frac{1}{\mathbf{h}\sqrt{\pi}};$$

therefore $$\mathbf{p} = 0{\cdot}8454\mathbf{a} \quad \text{or} \quad \mathbf{a} = 1{\cdot}18\mathbf{p}.$$

We can also show, by differentiating y twice with respect to x and equating to zero, that at the point of inflexion

$$x^2\mathbf{h}^2 = \tfrac{1}{2} \quad \text{but} \quad \mathbf{m}^2\mathbf{h}^2 = \tfrac{1}{2};$$

therefore $x = \mathbf{m}$ at the point of inflexion.

To use the probability tables to obtain estimates regarding a single observation, proceed thus. From a series of measurements, find $d_1, d_2, d_3, \ldots d_n$;

then $\mathbf{m}$ from $\mathbf{m}^2 = \dfrac{d_1^2 + d_2^2 + d_3^2 + \ldots d_n^2}{n-1}$

and $\mathbf{p}$ from $\mathbf{p} = 0{\cdot}6745\mathbf{m}$.

Suppose that we wish the range corresponding to a probability of 96 in 100 for example.

Against $\mathbf{P} = 0{\cdot}9603$ we find $\dfrac{x}{\mathbf{p}} = 3{\cdot}05$;

therefore $x = 3{\cdot}05 \times 0{\cdot}6745 \times \sqrt{\dfrac{d_1^2 + d_2^2 + d_3^2 + \ldots d_n^2}{n-1}}$.

We can, thus, be practically certain that a single measurement will give a value falling within the range of values, the highest of which is greater than the correct value by

$$3{\cdot}05 \times 0{\cdot}6745 \times \sqrt{\frac{d_1^2 + d_2^2 + d_3^2 + \ldots d_n^2}{n-1}}$$

and the lowest of which is less by the same amount, or a range about twice as wide as the range between the points of inflexion.

Similarly, we can find the range of values corresponding to any probability we please. For example, against $\mathbf{P} = 0{\cdot}9915$ we find $\dfrac{x}{\mathbf{p}} = 3{\cdot}9$ and against $\mathbf{P} = 0{\cdot}9990$, $\dfrac{x}{\mathbf{p}} = 4{\cdot}9$.

All the above errors have had reference to *single observations*. We must now consider how these errors contribute to the error of the *mean*. If n observations are made in order to obtain a mean and if each observation has a precision indicated

by a "**mean error**" equal to $\mathbf{m}$, then the resulting "**mean error**" *of the mean* equals $\frac{\mathbf{m}}{\sqrt{n}}$. Put $\frac{\mathbf{m}}{\sqrt{n}} = \mathbf{m}_M$. Similarly, corresponding to $\mathbf{a}$ we have $\frac{\mathbf{a}}{\sqrt{n}}$ or $\mathbf{a}_M$, and corresponding to $\mathbf{p}$ we have $\frac{\mathbf{p}}{\sqrt{n}}$ or $\mathbf{p}_M$.

To use the probability tables in studying the reliability of the mean, proceed thus: From the series of observations find d_1, d_2, $d_3 \ldots d_n$,

and then $\mathbf{m}$ from $\mathbf{m}^2 = \dfrac{d_1^2 + d_2^2 + d_3^2 + \ldots d_n^2}{n-1}$

and $\mathbf{p}_M$ from $\mathbf{p}_M = \dfrac{0{\cdot}6745}{\sqrt{n}} \sqrt{\dfrac{d_1^2 + d_2^2 + d_3^2 + \ldots d_n^2}{n-1}}$

Use the tables giving $\frac{x}{\mathbf{p}}$ or $\frac{x_M}{\mathbf{p}_M}$ and the corresponding value of the *Probability* $\mathbf{P}$, and suppose that we wish to know the *range of errors* which the mean may have corresponding to a probability of 97 in 100 (say). Against $\mathbf{P} = 0{\cdot}9701$ we find $\frac{x_M}{\mathbf{p}_M} = 3{\cdot}22$. Therefore

$$x_M = 3{\cdot}22 \times 0{\cdot}6745 \sqrt{\frac{d_1^2 + d_2^2 \ldots + d_n^2}{n(n-1)}}.$$

It is thus practically certain that the mean obtained will be *one of a range of values* the highest of which is greater than the correct value by

$$3{\cdot}22 \times 0{\cdot}6745 \sqrt{\frac{d_1^2 + d_2^2 + d_3^2 + \ldots d_n^2}{n(n-1)}}$$

and the lowest of which is less than the correct value by

$$3{\cdot}22 \times 0{\cdot}6745 \sqrt{\frac{d_1^2 + d_2^2 + d_3^2 + \ldots d_n^2}{n(n-1)}}.$$

This degree of certainty would satisfy most people. Indeed a less probability is sometimes used, for example,

$$0{\cdot}957, \quad \text{for which} \quad \frac{x_M}{\mathbf{p}_M} = 3,$$

and therefore

$$x_M = 3 \times 0{\cdot}6745 \sqrt{\frac{d_1^2 + d_2^2 + d_3^2 + \ldots d_n^2}{n(n-1)}}.$$

This is approximately numerically equal to $\frac{2\mathbf{m}}{\sqrt{n}}$.

Thus for 16 observations x_M would equal $\frac{\mathbf{m}}{2}$

and for 25 „ x_M „ „ $\frac{2\mathbf{m}}{5}$,

and the corresponding ranges are in the first case $\frac{1}{2}$ of the range between the points of inflexion on the *single-measurements* probability curve, and in the second case $\frac{2}{5}$ of that range. Thus, increasing the number of observations narrows the range within which a mean *must* be.

This is a theoretically correct way of estimating the greatest error practically possible for the mean. The chief objection to this method is the tedious calculation. What is frequently done in ordinary practice is to write the result $M \pm \mathbf{a}$, where M is the mean and **a** is the average of the deviations of the individual values from the mean, or

$$\mathbf{a} = \frac{d_1 + d_2 + d_3 + \ldots + d_n}{n},$$

all the deviations being written positive. Now, **a** is the **average error** of a *single measurement* and *has no direct reference to the mean*, and yet it is obviously used here as an indication of the greatest error (practically possible) to which the *mean* is liable. There seems to be here a confusion of ideas which is indefensible. There is, however, some justification for this usage of **a**. It has to be borne in mind that the probability of the **a-range** for a *single measurement* is only about $\frac{4}{7}$, whereas a range numerically equal to this but referring to errors of the *mean* has a probability which is much higher, and may even amount to practical certainty. If **a** is to be used to measure the reliability of M, then the probability (referred to M) of

the **a-range** should be high. Put $\mathbf{a} = x_M$ and find the probability of the x_M range. We have $x_M = \mathbf{a} = 1{\cdot}18\mathbf{p}$. In the tables we find the probabilities for various values of

$$\frac{x_M}{\mathbf{p}_M} \quad \text{or of} \quad \frac{1{\cdot}18\mathbf{p}}{\mathbf{p}/\sqrt{n}} \quad \text{or of} \quad 1{\cdot}18\sqrt{n}.$$

If $n = 5$, $\dfrac{x_M}{\mathbf{p}_M} = 1{\cdot}18 \times 2{\cdot}23 = 2{\cdot}63$ and $\mathbf{P} = 0{\cdot}9238$.

If $n = 9$, $\dfrac{x_M}{\mathbf{p}_M} = 1{\cdot}18 \times 3 = 3{\cdot}54$ and $\mathbf{P} = 0{\cdot}9831$.

If $n = 10$, $\dfrac{x_M}{\mathbf{p}_M} = 1{\cdot}18 \times 3{\cdot}16 = 3{\cdot}73$ and $\mathbf{P} = 0{\cdot}9881$.

If $n = 15$, $\dfrac{x_M}{\mathbf{p}_M} = 1{\cdot}18 \times 3{\cdot}87 = 4{\cdot}57$ and $\mathbf{P} = 0{\cdot}9979$.

If $n = 25$, $\dfrac{x_M}{\mathbf{p}_M} = 1{\cdot}18 \times 5 = 5{\cdot}90$ and $\mathbf{P} = 0{\cdot}9999$.

Thus this method does yield an *error-range* of very high probability, provided (say) $n = 10$ upwards and the probability becomes greater the greater the number of observations. The probability when $n = 25$ is so great that in using this method there seems no need to go beyond this figure. We must, however, fix upon one probability to be adhered to in comparing errors, and therefore in this method we would require to fix upon one value of n. In the other method, the probability $\mathbf{P} = 0{\cdot}957$ may be selected and all errors determined on this basis, when $\dfrac{x_M}{\mathbf{p}_M}$ is always equal to 3, or $\mathbf{P} = 0{\cdot}9990$ (say) may be chosen when $\dfrac{x_M}{\mathbf{p}_M} = 4{\cdot}9$.

The conditions necessary for the application of the above theory of errors are that all the measurements are equally likely to be in error, and that we are dealing only with the chance or fortuitous errors, called errors of observation, also that there have been a large number of measurements. If the conditions are not satisfied, quite misleading results

may be obtained. With physical and chemical observations, where we can have the conditions largely under control, it is not necessary to have so many measurements as would otherwise be required. In the above "*average error*" method of estimating the reliability of the mean it was shown that when $n = 10$, the probability that the error of the mean is within the a-*range* is almost 99 in 100, and when $n = 25$, the probability is 9999 in 10,000. In ordinary practice, 25 observations are considered more than sufficient, and something between that figure and 10 is usually held to be all that is required. The more we reduce n, however, the less valid does the application of the theory become. If $n = 10$, the formulae yield only approximate values, and if used in the ordinary form give to the method of calculation an appearance of far greater accuracy than we can claim for it. Thus, we can substitute $\frac{2}{3}$ for 0·6745 in the above without reducing the accuracy of the formulae, and also for other decimals in the formulae similar substitutions may be made, when n is small.

In many cases we can make only a *single measurement* of a quantity. Similar determinations, therefore, must have already been carried out either by ourselves or by others if we are to form some estimate of the error of the single measurement and of the corresponding error in any result depending on that measurement. If the error-value given in the records of similar experiments is really the value of a (as is often the case), then we must multiply this value by at least 2·5 to obtain the greatest error (practically possible) for a *single measurement*.

Errors in the Measurement of Certain Commonly Occurring Quantities.

There are mentioned here errors of fundamental quantities frequently involved in the calculation of the result of an experiment and therefore errors contributing to the error of

Errors in the Measurement of Certain Commonly Occurring Quantities.

Quantity.	Remarks.	Order of Absolute Error.	Order of Relative Error.
Weight			
Standard Kilogram	Very refined method	± 0.000002 gram	$\pm 2 \times 10^{-9}$
Weight as usually measured	With ordinary analytical balance	± 0.0001 to ± 0.0002 gram	To obtain $\pm 0.1\%$ at least 0·1 to 0·2 gram should be weighed
Atomic Weights	See Table of Atomic Weights	From ± 0.0005 for hydrogen to ± 1.0 for tantalum thulium and ytterbium	All $> \pm 10^{-4}$ Some $= \pm 10^{-3}$ Most $> \pm 10^{-3}$
Length			
Standard Metre	Very refined method	$\pm 2 \times 10^{-7}$ metre	$\pm 2 \times 10^{-7}$
Metre column of Mercury	Very refined method	$\pm 10^{-6}$ metre	$\pm 10^{-6}$
Length scale readings as usually measured	With unaided eye avoiding parallax With Vernier With common form of micrometer screw	± 0.1 mm. ± 0.05 to ± 0.02 mm. ± 0.001 mm.	
Reading of scale of Burette	Where 1 c.c. is equivalent to rather more than 1 cm. length of scale	± 0.01 c.c.	

Angle	Error really depends on error in measurement of a length		
	Refractometer		
	With Vernier	$\pm \frac{1}{60}°$ or $\pm 0.016°$	
	With Micrometer Screw	$\pm 0.002°$	
	Polarimeter·		
	With Vernier	$\pm 0.01°$	
Volume			
Standard Volume			
Volume of 1 gram of Water at 4° C.	Volume is now known to be 1·00003 c.c.	± 0.00002	± 0.002 %
			Deviation from 1 c.c. is ± 0.003 %
Usual volume determination:	Error due to influence of temperature, pressure and lag of thermal changes in volume of vessel		Almost always $> \pm 0.01$ %
With Pipette	Diameter of upper tube / Volume of pipette		
	1 mm. / 1 c.c.	About ± 0.0005 c.c.	About ± 0.05 %
	3 mm. / 10 c.c.	About ± 0.005 c.c.	About ± 0.05 %
	8 mm. / 100 c.c.	About ± 0.05 c.c.	About ± 0.05 %
With Burette	See under Measurement of Length. Volume = difference between two scale readings	Usually about ± 0.014 c.c.	To obtain ± 0.1 % at least 14 c.c. should be taken
With Graduated Flask	Diameter in mm. of neck of flask $= 2\sqrt[3]{V}$ c.c., where V = capacity of flask.		± 0.05 %

ERRORS IN THE MEASUREMENT OF CERTAIN COMMONLY OCCURRING QUANTITIES—*Continued.*

QUANTITY.	REMARKS.	Order of Absolute Error.	Order of Relative Error.
Density of Liquids			
With Pyknometer	Volume of Pyknometer = 5 c.c. Accuracy rises if volume is increased until about 30 c.c. is reached, above which errors due to temperature diminish accuracy.	±0·0001	Usually about ±0·01 %
With Ordinary Pipette (10 to 100 c.c.)	Pipette is filled with liquid and contents are weighed in a tared vessel. Similarly for water.	±0·001	Usually about ±0·1 %
Westphal Balance		±0·0005	Usually about ±0·05 %
Floats	Useful in detecting very small differences in density	±0·000001 to ±0·000002	
Density of Solids			
With Burette	Measuring volume of liquid displaced by solid. Error with 1 c.c. displaced. (Relative error inversely proportional to volume displaced)		±2 %
With Pyknometer Flask (with perforated stopper)	Error with 1 c.c. displaced (Relative error inversely proportional to volume displaced)		±0·1 %

Temperature			
Standard Temperatures	See List of Standard Temperatures used in calibration	From ±0·1° in M.P. of Cd and of Zn to ±5·0° in M.P. of Pt	From ±0·03 % to nearly ±0·3 %
Refined Methods	By refined methods, mercury, gas, resistance and thermo-couple thermometers have accuracies approximately equal wherever they can be applied		
	Least error		
	From 0° to 100°	±0·005°	
	Near 200	±0·01°	
	300	±0·03°	
	400	±0·1°	
	500	±0·2°	
	1000	±1·0°	
Ordinary Methods	Laboratory Mercury Thermometer		
	If corrected and checked		
	From 0° to 100°	±0·02°	
	Near 200°	±0·05°	
	400°	±0·5°	
	If not corrected		
	From 0° to 100°	Several tenths of a degree	
	At higher temps.	Several degrees	
Measurement of Small Differences	Beckmann divided into hundredths of a degree	±0·001°	To obtain ±1 % at least 0·1° should be measured
	Most accurate Mercury Thermometer	±0·0002°	
	Electrical Method (0° to 100°)	±0·000001°	

ERRORS IN THE MEASUREMENT OF CERTAIN COMMONLY OCCURRING QUANTITIES—*Continued.*

QUANTITY.	REMARKS.	Order of Absolute Error.	Order of Relative Error.
Electrical Measurements			
Refined Methods	Resistance, current and E.M.F. can be measured in terms of international units with the accuracy mentioned		$\pm 5 \times 10^{-5}$
Resistance Standards for Ordinary Work	A convenient box containing resistances from 1 ohm to 5000 ohms can be obtained having throughout at most the relative error mentioned		$\pm 0{\cdot}1\ \%$
Standard E.M.F.	Comparison of Weston Cells		Few units $\times 10^{-5}$
Measurement of E.M.F. by Ordinary Methods		From $\pm 0{\cdot}0001$ volt to $\pm 0{\cdot}00001$ volt	$\pm 10^{-5}$
Electro-chemical equivalent of silver			

that result. Some of these quantities have to be measured in the course of the experiment by ordinary methods, and the errors are comparatively large. Some, on the other hand, have already been measured by very refined methods (for example, standard weights), and it would not usually be considered necessary to measure them again; the error here is often comparatively small.

It may be objected, that some of the errors given here are rather low for ordinary work, and certainly this may be the case, for example, when several persons are working in the same room. Therefore, in laboratory teaching we must be content in some cases with errors slightly higher than those mentioned.

It will be seen that few physical quantities have an error less than $\frac{1}{1000}$; therefore their value is usually expressed by a number of not more than 4 digits, of which the last digit is uncertain and obtained by rounding off. For example, in 4·543 the digit 3 is uncertain, and the number 4·543 may have been the result of rounding off 4·5425 or any number between 4·5425 and 4·5435. If a value has an error of the order 1 in 1000 and is expressed by 5 digits, the last digit is misleading, implying as it does that the error is of the order 1 in 10,000. The accuracy of 1 in 1000 is more than sufficient for most purposes.

In ordinary arithmetic, to indicate the position of the decimal point it may be necessary to put one or more zeros at the beginning or at the end of a number. The method adopted in physical arithmetic will be understood from the following:

45,360,000 is expressed as $4{\cdot}536 \times 10^7$ when 6 is the first uncertain digit; $4{\cdot}5360 \times 10^7$ would mean that 6 was certain and 0 uncertain. 0·004536 is expressed as $4{\cdot}536 \times 10^{-3}$ when 6 is the only uncertain digit.

The Effect of Errors in Fundamental Quantities on the Error of a Calculated Result.

The calculation of this effect is of importance not only that we may measure correctly the degree of uncertainty in the result, but also that we may see how each fundamental measurement contributes to that uncertainty, and so may ascertain whether any of the observations require to be carried out with greater care than the others if all are to contribute equally to the error in the result.

In dealing with **errors of observation** *we are considering ranges of errors, and we must adhere to the same probability throughout a calculation.* Thus, if we use the **m**-*range* for one fundamental quantity, then we must use the **m**-*range* for all the other fundamental quantities, and the calculation gives the **m**-*range* of the result. Similarly, we might choose to calculate with the **a**-*range* or with the **p**-*range*, or we might select the probability 96 in 100 (say) and work with the corresponding range.

When we are considering **constant errors** in fundamental quantities and wish to calculate the corresponding error in the result, then we are not studying ranges of errors, and the question of probability does not enter.

Let $X=f(A, B)$, *i.e.* let X equal an expression containing the quantities A and B which are subject to error and, it may be, other quantities not subject to error.

If dA is a small change (error) in A, then the error in X is $\frac{\partial f}{\partial A}dA$, provided that there are no other sources of error.

Similarly, a small change (error) dB in B gives rise to $\frac{\partial f}{\partial B}dB$.

If dA is a **constant error** in A and dB is a constant error in B, the total resulting error in X is $\frac{\partial f}{\partial A}dA+\frac{\partial f}{\partial B}dB$, or the errors are simply algebraically additive.

Now, *if we are dealing with* **errors of observation** *or* **chance errors**, *then we consider ranges of errors and not single errors* as in the above. Thus, in connection with A we consider a range of errors from $+dA$ to $-dA$, the probability of this range being, we shall suppose, $\frac{1}{2}$. The probability is $\frac{1}{2}$ that the error in A is within this range, and the probability would be $\frac{1}{2}$ that the error in X is within the range from $+\frac{\partial f}{\partial A}dA$ to $-\frac{\partial f}{\partial A}dA$, provided that there are no other sources of error.

Similarly, if B alone were contributing to the error in X, then the probability is $\frac{1}{2}$ that the error in X is within the range from $+\frac{\partial f}{\partial B}dB$ to $-\frac{\partial f}{\partial B}dB$, provided that for B the probability is $\frac{1}{2}$ for the range of errors from $+dB$ to $-dB$.

Thus, if we suppose throughout that we are dealing with ranges of the same probability (not necessarily $\frac{1}{2}$), then the range of errors $\pm dA$ in A by itself leads to $\pm\frac{\partial f}{\partial A}dA$ in X and $\pm dB$ in B by itself leads to $\pm\frac{\partial f}{\partial B}dB$ in X; but $\pm dA$ and $\pm dB$ acting together do not lead to $\pm\left(\frac{\partial f}{\partial A}dA+\frac{\partial f}{\partial B}dB\right)$, but to a narrower range. We must consider not only possible cases where a positive error in A acts along with a positive error in B or a negative error in A along with a negative error in B, but also possible cases where a positive error in A acts along with and may even neutralise a negative error in B, and vice versa. It can be shown that in X the range of errors the probability of which is the same as the probability of $\pm dA$ and $\pm dB$ is given by the equation

$$(dX)^2=\left(\frac{\partial f}{\partial A}dA\right)^2+\left(\frac{\partial f}{\partial B}dB\right)^2,$$

or

$$dX=\pm\sqrt{\left(\frac{\partial f}{\partial A}dA\right)^2+\left(\frac{\partial f}{\partial B}dB\right)^2}.$$

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Thus, in general, if $X = f(A, B, C, D, \ldots)$;

then **for constant errors**:

$$dX = \frac{\partial f}{\partial A}dA + \frac{\partial f}{\partial B}dB + \frac{\partial f}{\partial C}dC + \ldots,$$

and **for ranges of errors all of the same probability**:

$$(dX)^2 = \left(\frac{\partial f}{\partial A}dA\right)^2 + \left(\frac{\partial f}{\partial B}dB\right)^2 + \left(\frac{\partial f}{\partial C}dC\right)^2 + \ldots,$$

or
$$dX = \pm\sqrt{\left(\frac{\partial f}{\partial A}dA\right)^2 + \left(\frac{\partial f}{\partial B}dB\right)^2 + \left(\frac{\partial f}{\partial C}dC\right)^2 + \ldots}.$$

It will thus be seen that *when there is only one fundamental quantity, the calculations for* **constant errors** *and for* **errors of observation** *are the same. When there are two or more fundamental quantities, the methods of calculation are different.* With constant errors we simply add algebraically the errors due to the fundamental quantities, but with ranges of errors of observation of the same probability we add the squares of the range-limits due to the fundamental quantities, and thus obtain the square of the range-limit in the result.

One Fundamental Quantity.

The area of a circle is given by $X = \pi R^2$, where R = the radius of the circle.

$$dX = \frac{\partial X}{\partial R}dR = 2\pi R\,dR.$$

For constant errors: $dX = 2\pi R\,dR$,

and **for ranges of errors of observation**: $dX = \pm 2\pi R\,dR$.

For relative errors: $$\frac{dX}{X} = \frac{2\pi R\,dR}{\pi R^2} = \frac{2dR}{R}.$$

Thus, if the *relative constant error* in R is 0·2 %, then the resulting error in the area is 0·4 %.

Again, if the *range of relative errors of observation* is expressed as ±0·2 % for R, then the degree of uncertainty in the result is expressed by ±0·4 % on the basis of the same probability.

Thus, when there is only one fundamental quantity, the calculations may agree numerically though the meaning of the numbers with the two kinds of errors is entirely different. This calculation shows that if we wish to obtain for the area a value whose relative error is within a certain range, then we are restricted to only half that error-range in the measurement of the radius (*on the basis of the same probability*).

Two or More Fundamental Quantities.

The volume of a circular cylinder is given by $X = \pi R^2 H$, where R = radius and H = height.

$$\frac{\partial X}{\partial R} dR = 2\pi R H\, dR, \quad \frac{\partial X}{\partial H} dH = \pi R^2 dH.$$

For constant errors: $dX = 2\pi R H\, dR + \pi R^2 dH,$

or expressed as relative errors: $\dfrac{dX}{X} = \dfrac{2\pi R H\, dR + \pi R^2 dH}{\pi R^2 H}$

$$= \frac{2dR}{R} + \frac{dH}{H},$$

or relative constant error in $X = 2 \times$ relative error in R + relative error in H.

Thus any relative error present in R has its effect doubled in the result, and therefore special care is required in the measurement of R.

For ranges of errors of observation:

$$dX = \pm\sqrt{(2\pi R H\, dR)^2 + (\pi R^2 dH)^2}.$$

As will be seen from the above, it is simpler to work with relative errors in considering a product.

$$X = \pi R^2 H, \quad \log X = \log \pi + 2 \log R + \log H,$$

$$d(\log X) = \frac{dX}{X}, \quad \frac{\partial(\log X)}{\partial(\log R)} d(\log R) = 2d(\log R) = \frac{2dR}{R},$$

$$\frac{\partial(\log X)}{\partial(\log H)} d(\log H) = d(\log H) = \frac{dH}{H},$$

$$[d(\log X)]^2 = \left[\frac{\partial(\log X)}{\partial(\log R)}\, d(\log R)\right]^2 + \left[\frac{\partial(\log X)}{\partial(\log H)}\, d(\log H)\right]^2,$$

or $$\left(\frac{dX}{X}\right)^2 = \left(\frac{2dR}{R}\right)^2 + \left(\frac{dH}{H}\right)^2,$$

or $$\frac{dX}{X} = \pm\sqrt{\left(\frac{2dR}{R}\right)^2 + \left(\frac{dH}{H}\right)^2}.$$

Thus a relative error of observation in the measurement of R still produces a greater effect on the result than does an equal relative error in the measurement of H, though not so great an effect as when constant errors are being studied.

If a relative error-range of $\pm 3\,\%$ is desired in the result, and if the fundamental measurements are to share equally in contributing to that error-range, then

$$\left(\frac{2dR}{R}\right)^2 = \left(\frac{dH}{H}\right)^2 = \frac{(0{\cdot}03)^2}{2}.$$

Therefore $\left(\frac{dR}{R}\right)^2$ must equal $\frac{(0{\cdot}03)^2}{4\times 2}$ or $\frac{dR}{R} = \pm 1{\cdot}06\,\%$,

and $\left(\frac{dH}{H}\right)^2$ must equal $\frac{(0{\cdot}03)^2}{2}$ or $\frac{dH}{H} = \pm 2{\cdot}12\,\%$.

Some Simple Cases.

Let a, b, c, d, ... be *constant errors* in A, B, C, D, ..., and let the resulting error in X be x. In dealing with *errors of observation* let these same letters be the *limits of ranges of errors* all of the same probability, the ranges being expressed as $\pm a$, $\pm b$, $\pm c$, $\pm d$, etc., and $\pm x$.

Cases of Addition and Subtraction.

Let $X = kA + lB$ (k and l are error-free);

then $$\frac{\partial X}{\partial A}\, dA = k\, dA = ka, \quad \frac{\partial X}{\partial B}\, dB = l\, dB = lb$$

For constant errors: $x = ka + lb$.

For ranges of errors of observation:

$$x^2=(ka)^2+(lb)^2 \quad \text{or} \quad x=\pm\sqrt{k^2a^2+l^2b^2}.$$

Let $$X=kA-lB;$$

then $$\frac{\partial X}{\partial A}dA=k\,dA=ka, \quad \frac{\partial X}{\partial B}dB=-l\,dB=-lB.$$

For constant errors: $x=ka-lb.$

For ranges of errors of observation:

$$x^2=(ka)^2+(-lb)^2 \quad \text{or} \quad x=\pm\sqrt{k^2a^2+l^2b^2}.$$

Let $$X=kA+lB+mC+qD+\ldots;$$

then **for constant errors:** $x=ka+lb+mc+qd+\ldots.$

For ranges of errors of observation:

$$x^2=k^2a^2+l^2b^2+m^2c^2+q^2d^2+\ldots,$$

or $$x=\pm\sqrt{k^2a^2+l^2b^2+m^2c^2+q^2d^2+\ldots}.$$

By this formula we can obtain also the error of a mean. Let $M=\frac{A+B+C+D+E}{5}$. M is the arithmetical mean of A, B, C, D and E. Let these five quantities all be measured with the same precision indicated by $\pm a$. Let the corresponding error-range in M be $\pm m$.

$$M=\frac{A}{5}+\frac{B}{5}+\frac{C}{5}+\frac{D}{5}+\frac{E}{5}.$$

Therefore $$m^2=\frac{a^2}{5^2}+\frac{a^2}{5^2}+\frac{a^2}{5^2}+\frac{a^2}{5^2}+\frac{a^2}{5^2},$$

or $$m^2=\frac{5a^2}{5^2}=\frac{a^2}{5} \quad \text{or} \quad m=\pm\frac{a}{\sqrt{5}}.$$

In general, if $M=\frac{A+B+C+D+\ldots \text{ to } n \text{ terms}}{n}$ and A, B, C, etc., are all measured with the same precision expressed by $\pm a$, then $m=\pm\frac{a}{\sqrt{n}}$.

Cases of Multiplication and Division.

In addition and subtraction absolute errors may be considered, but in multiplication and division it is more convenient to calculate with relative errors.

Let a, b, c, d, ... be now relative constant errors in A, B, C, D, ..., and let the resulting relative error in X be x. In dealing with *ranges of errors of observation*, let these same letters be the *limits of ranges of relative errors all of the same probability*, the ranges being expressed as $\pm a$, $\pm b$, $\pm c$, etc., and $\pm x$.

Let $X = nAB$ (n is error-free);

then $$\log X = \log n + \log A + \log B,$$

$$d(\log X) = \frac{dX}{X},$$

$$\frac{\partial(\log X)}{\partial(\log A)} d(\log A) = d(\log A) = \frac{dA}{A},$$

$$\frac{\partial(\log X)}{\partial(\log B)} d(\log B) = d(\log B) = \frac{dB}{B}.$$

For constant errors: $\frac{dX}{X} = \frac{dA}{A} + \frac{dB}{B} = a + b.$

For ranges of errors of observation:

$$\left(\frac{dX}{X}\right)^2 = \left(\frac{dA}{A}\right)^2 + \left(\frac{dB}{B}\right)^2,$$

or $$x^2 = a^2 + b^2 \quad \text{or} \quad x = \pm\sqrt{a^2 + b^2}.$$

Let $X = n\frac{A}{B}$ (n is error-free);

then $$\log X = \log n + \log A - \log B,$$

$$d(\log X) = \frac{dX}{X},$$

$$\frac{\partial(\log X)}{\partial(\log A)} d(\log A) = d(\log A) = \frac{dA}{A},$$

$$\frac{\partial(\log X)}{\partial(\log B)} d(\log B) = -d(\log B) = -\frac{dB}{B}.$$

For constant errors: $\frac{dX}{X} = \frac{dA}{A} - \frac{dB}{B}$ or $x = a - b$.

For ranges of errors of observation:

$$\left(\frac{dX}{X}\right)^2 = \left(\frac{dA}{A}\right)^2 + \left(\frac{dB}{B}\right)^2,$$

or $x^2 = a^2 + (-b)^2 = a^2 + b^2$ or $x = \pm\sqrt{a^2 + b^2}$.

Let $X = n\frac{A^l B^m}{C^q}$, (n, l, m and q are error-free);

then $\log X = \log n + l \log A + m \log B - q \log C$,

$$d(\log X) = \frac{dX}{X}, \quad \frac{\partial(\log X)}{\partial(\log A)} d(\log A) = l\, d(\log A) = l\frac{dA}{A},$$

$$\frac{\partial(\log X)}{\partial(\log B)} d(\log B) = m\, d(\log B) = m\frac{dB}{B},$$

$$\frac{\partial(\log X)}{\partial(\log C)} d(\log C) = -q\, d(\log C) = -q\frac{dC}{C}.$$

For constant errors:

$$\frac{dx}{x} = l\frac{dA}{A} + m\frac{dB}{B} - q\frac{dC}{C},$$

or $x = la + mb - qc$.

For ranges of errors of observation:

$$\left(\frac{dX}{X}\right)^2 = \left(l\frac{dA}{A}\right)^2 + \left(m\frac{dB}{B}\right)^2 + \left(-q\frac{dC}{C}\right)^2,$$

or $x^2 = l^2a^2 + m^2b^2 + q^2c^2$,

or $x = \pm\sqrt{l^2a^2 + m^2b^2 + q^2c^2}$.

Example of the above form: In the determination of the molecular weight by depression of the freezing point, we use the relation $M = \frac{w \times 100 \times t_m}{W \times d}$, where M = mol. wt., w = weight of solute and W = weight of solvent. Thus for ranges of errors of observation, we have

rel. error in M

$= \pm\sqrt{(\text{rel. error in } w)^2 + (\text{rel. error in } W)^2 + (\text{rel. error in } d)^2}$,

and for constant errors

rel. error in M = rel. error in w − rel. error in W − rel. error in d.

Summary of some of the Above Formulae.

Addition and Subtraction. (Here a, b, c, ... refer to *absolute errors*):

Forms of X.	Constant Errors.	Errors of Observation.
$X = kA + lB$	$x = ka + lb$	$x = \pm\sqrt{k^2a^2 + l^2b^2}$
$X = kA - lB$	$x = ka - lb$	$x = \pm\sqrt{k^2a^2 + l^2b^2}$
$X = kA + lB + mC + \ldots$	$x = ka + lb + mc + \ldots$	$x = \pm\sqrt{k^2a^2 + l^2b^2 + m^2c^2 + \ldots}$

Multiplication and Division. (Here a, b, c, ... refer to *relative errors*):

Forms of X.	Constant Errors.	Errors of Observation.
$X = nAB$	$x = a + b$	$x = \pm\sqrt{a^2 + b^2}$
$X = n\dfrac{A}{B}$	$x = a - b$	$x = \pm\sqrt{a^2 + b^2}$
$X = \dfrac{nA^lB^m}{C^q}$	$x = la + mb - qc$	$x = \pm\sqrt{l^2a^2 + m^2b^2 + q^2c^2}$

The best method of obtaining these results is by using the general differential formulae referred to above, which are applicable to any form of X, but the above table will be found useful by those unable to apply the differential calculus.

As a further illustration of the above, consider $X = A - B$,

where $A = 12{\cdot}5431 \pm 0{\cdot}0003$ grams

and $B = 12{\cdot}3421 \pm 0{\cdot}0002$ grams,

$X = 0{\cdot}2010 \pm x$.

All these are *ranges of absolute errors of observation*,

and $x = \pm\sqrt{(0{\cdot}0003)^2 + (0{\cdot}0002)^2} = \pm 0{\cdot}00036$.

On the other hand, if the errors were *constant errors*, then x would equal $0{\cdot}0003 + 0{\cdot}0002$ or $0{\cdot}0005$. In the case of *ranges of errors of observation* we are dealing with a problem in probability, and we have to consider not only the possible cases where two positive errors affect the result simultaneously, but

also the possible cases where a positive and a negative error may act together, and may even neutralise one another, giving a result with no error. Thus we obtain as the range of errors of the same probability in the result $\pm 0{\cdot}00036$ instead of the single error $0{\cdot}0005$ obtained when constant errors are considered.

This means that for X the range of errors $\pm 0{\cdot}00036$ has the *same probability* as the range $\pm 0{\cdot}0003$ for A and $\pm 0{\cdot}0002$ for B. Thus, if the range $\pm 0{\cdot}0003$ for A has a probability of 96 in 100, and therefore also the range $\pm 0{\cdot}0002$ for B has a probability of 96 in 100, then for X the range $\pm 0{\cdot}00036$ must have the probability 96 in 100. What is insisted upon is that the probabilities of the ranges for A and B should be the same, not necessarily the values of these ranges. To emphasise this point, the ranges for A and B have been supposed of different values, though in practice the values would here be the same, say, $\pm 0{\cdot}0002$.

Again, suppose that in reading the scale of a burette the error of observation is $\pm 0{\cdot}01$ c.c., then the error in a volume measurement (which is equal to the difference of two scale readings) is $\pm\sqrt{(0{\cdot}01)^2+(0{\cdot}01)^2}$ or $\pm 0{\cdot}0142$ c.c. Note that here any personal error (which is usually regarded as constant) is cancelled when the same person takes both readings.

The Arithmetic of Numbers expressing Approximate Values.

The value of no physical quantity is known exactly ; therefore in Physical Arithmetic we have to operate with digits some of which are uncertain. To go further than the first uncertain digit in a number is not only to express the value in a form which is misleading, but also to increase unnecessarily the labour of calculation. Whenever an arithmetical operation carried out in the ordinary way would yield (in the result or at any intermediate step) a number having several digits beyond the first uncertain digit, then the calculation should be modified in such a way as to yield no digits beyond the first uncertain digit. An extra digit may, however, be retained if the result is to be employed in further calculations, but this extra digit is added only for use in this way.

Here again, *in addition and subtraction absolute errors should be considered, and in multiplication and division relative errors.* It should be borne in mind, for example, that in the **addition and subtraction** of numbers, the absolute errors in the result will be of the order of the greatest absolute error present among the numbers taking part in the operation.

If the actual errors of the numbers taking part in an operation are not specified, then the *apparent errors* must be determined on the assumption the numbers have been obtained by rounding off according to the usual rules. Thus, in the addition

$$\begin{array}{r} 527{\cdot}4 \\ 0{\cdot}8572 \\ \hline 528{\cdot}2572 \end{array}$$

in 527·4 the digit 4 is uncertain, and may have been obtained by *rounding off* from 527·35 or any number between 527·35 and 527·45. Thus, 527·4 have an *apparent absolute error* of $\pm 0{\cdot}05$. The *apparent absolute error* in 0·8572, on the other hand, is $\pm 0{\cdot}00005$. The *apparent absolute error* in the result is, therefore, of the order $\pm 0{\cdot}05$, and there is no need for so many digits in the result, which should be written 528·3, and the same number would have been obtained by rounding off the number 0·8572 still further to 0·857 or even to 0·86.

Again, in **multiplication and division** the relative error in the result will be of the order of the greatest relative error present among the numbers taking part in the operation. For example, if both the numbers in the product $1{\cdot}537 \times 3{\cdot}42$ are numbers containing errors, then the relative error of the product will be of the order of the relative error in 3·42, which is the more inaccurate number. The product should therefore be expressed by a number containing only 3 digits. In other words, the number of digits in the result should be the same as that in the factor containing the fewest digits, if factors which are not subject to error are not considered. In applying this rule, a factor containing 2 digits the first of which is 5 or more must

be regarded as a factor of 3 digits, a factor containing 3 digits the first of which is 5 or more must be regarded as a factor of 4 digits, and so on. The rule must be modified in the same way in settling how many digits to give in a result. If the product begins with 5 or more, then one digit less is required than if the product begins with 4 or less.

In illustration of the above rules note the following:

$$1{\cdot}237 \times 3{\cdot}42 = 4{\cdot}23054$$

when worked out in the ordinary way. The factor 3·42 contains the fewest digits; therefore only 3 digits should be retained in the result, which should be written 4·23. For use in further calculation it may be written 4·231.

Again, $9{\cdot}7 \times 1{\cdot}32 = 12{\cdot}804$. Here 9·7 contains the fewest digits, but as it begins with 9 it must be regarded as a factor containing 3 digits, and 3 digits must be retained in the result, which should be written 12·8. For use in further calculation it may be written 12·80.

Multiplication carried out in the ordinary way, therefore, yields too many digits. To avoid unnecessary labour, a shortened method may be employed in which the number of digits at each step in the operation is restricted, the last digit being obtained by rounding off from the digits rejected. Also, logarithm tables may be used, having one more place than the most inaccurate factor contains, and the proper number of digits will then be automatically maintained.

Similar remarks may be made regarding division.

Aids to Calculation.

Reference has already been made to **logarithms**, and whether tables are employed or a slide-rule an error is always involved. The error of 4-place logarithm tables is at most 1 in 3000 and of 5-place logarithm tables 1 in 30000. The error of a slide-rule about 25 cms. long is 2 in 1000. For most of the work in this book 4-place logarithms will be sufficient.

Constant Errors.

As indicated above, the reliability of a mean can be determined on the basis of any probability we please. If after having calculated the reliability of a mean we keep to the same probability and determine the reliability of a second mean as found by a second method of measuring the same quantity, we may find that there is a discrepancy between the two means far greater than can be accounted for by the uncertainty of each. This is a most important application of the theory of errors. A classical example was the discrepancy observed between the density of nitrogen as prepared from ammonia and the density of nitrogen as prepared from air. The discrepancy could not be explained by the degree of uncertainty of each density, and led to the discovery of argon. There was present in the second experiment (with nitrogen from air) not only the **error of observation** but also a **constant error** due to the presence of impurity.

As a further illustration, suppose that the electrical conductivity of a liquid is measured by comparison with the conductivity of a standard liquid. If the conductivity of the standard is not known correctly, then, no matter how precise the experimental method, the result will have a constant error which may be comparatively great. *A* **constant error** *affects all the values obtained to the same extent and in the same direction.* The presence of a constant error may often be detected by varying the conditions, for example, in the case mentioned, by changing the standard liquid. Measurements in which a second standard liquid is used may yield a second set of values which, though they differ from one another on account of the *error of observation*, yet have all the same *constant error*, which, however, will probably differ from the constant error with the first standard liquid. If the constant errors obtained with the two standard liquids are different, this will be indicated by the mean of the first series of values being different from

the mean of the second series by an amount which is greater than can be accounted for by the errors of the different means. Space will not permit entering further into the details of the method for measuring constant errors.

A **personal error** is a form of *constant error* which can be detected by comparing the results obtained by different persons when they are measuring the same quantity. For example, in measuring a length with the unaided eye the scale gives the value to mms., but when we come to fractions of a mm. an estimate has to be formed, and two persons may have different opinions as to what fraction of a mm. should be given in the reading. The uncertainty due to a personal error can be measured by comparing the readings of a large number of persons; the personal errors then assume the nature of chance errors or errors of observation: some may lead to results greater than the correct value, some to results less, and it is just as likely to be one way as the other. Thus the methods of the theory of errors become applicable, and the same holds for other forms of constant error when the conditions are varied sufficiently.

The Definition of the Object.

When a volatile liquid is weighed in an open vessel, the loss due to evaporation during the weighing may be so great that we can give the weight only to the first or second decimal place. We say that the **definition of the object** is bad. In a case like this, to use a balance weighing to the fourth decimal place is an unscientific and futile proceeding. A similar truth holds for other measurements. For example, it would be useless to measure by a very refined method the conductivity of a solution the concentration of which is undergoing a more or less rapid change.

The Weighting of Measurements.

When a series of values, A, B and C, obtained in an observation of the same quantity are all equally reliable, then the value which best represents the data is given by

$$M = \frac{A+B+C}{3}.$$

But when A, B and C are not equally reliable, we speak about assigning different **weights** to each. The more reliable a value is the higher do we **weight** it. If we reject a value the weight is zero. Thus, for example, we might weight A, B and C in the proportion $4:1:3$, implying that A is the most reliable and B the least. The most probable value then is given by

$$M = \frac{4A+B+3C}{4+1+3} = \frac{4A+B+3C}{8}.$$

Similarly a series of means may be obtained of different reliabilities, and a *general mean* calculated after weighting the *individual means*. Thus, for example, the "**mean error**" or the "**probable error**" is sometimes taken as a guide in comparing the reliabilities of the different means. Let the *probable errors* of the means X, Y and Z be x, y and z; then the "*weights*" are as $\frac{1}{x^2}$, $\frac{1}{y^2}$, $\frac{1}{z^2}$, and the

$$\textbf{general mean} = \frac{\frac{X}{x^2}+\frac{Y}{y^2}+\frac{Z}{z^2}}{\frac{1}{x^2}+\frac{1}{y^2}+\frac{1}{z^2}}.$$

(For a proof of this formula see below.)

There is a considerable difference of opinion as to what is the best method of weighting. In atomic weight calculations, for example, it has been thought by Meyer and Seubert, and others, that the weighting should be in proportion to the quantity of substance used in the experiment. F. W. Clarke, on the other hand, used the "*probable error*" method. Morley,

in his work on the densities of oxygen and hydrogen, judged each case by experimental evidence and weighted accordingly. "*Weighting*" is, on the whole, a very unsatisfactory process, the choice of "*weights*" being often largely of an arbitrary nature.

If an observation has a "weight" w we mean that it is equivalent to w observations each of weight unity. If the "*probable error*" of the observations of unity weight is $\mathfrak{q}$ and the "*probable error*" of an observation of weight w_1 is $\mathfrak{p}_1$, then (see above under "probable error of a mean")

$$\mathfrak{p}_1 = \frac{\mathfrak{q}}{\sqrt{w_1}} \quad \text{or} \quad \mathfrak{p}_1^2 = \frac{\mathfrak{q}^2}{w_1} \quad \text{or} \quad w_1 = \frac{\mathfrak{q}^2}{\mathfrak{p}_1^2}.$$

Similarly for the weights w_2, w_3, etc., we obtain

$$w_2 = \frac{\mathfrak{q}^2}{\mathfrak{p}_2^2}, \quad w_3 = \frac{\mathfrak{q}^2}{\mathfrak{p}_3^2}, \quad \text{etc.}$$

Therefore $$w_1 : w_2 : w_3 = \frac{1}{\mathfrak{p}_1^2} : \frac{1}{\mathfrak{p}_2^2} : \frac{1}{\mathfrak{p}_3^2}.$$

Though this method of weighting appears to be less arbitrary than the others, and therefore more satisfactory, yet it may yield quite misleading results, especially if constant errors are present large compared with the errors of observation.

EXERCISE 1.

Determination of Density of Carbon Dioxide (Weighing Method).

A thick-walled flask is used, provided with a ground-in stopper *II* (see Fig. 3), which is hollow and is perforated with a hole, which when placed opposite the side tube **A** acts as an inlet; any gas entering at **A** passes in at this hole and down a tube to the bottom of the flask. This tube **A** is connected by pressure rubber tubing with a calcium chloride tube, so that gases may be dried as they enter.

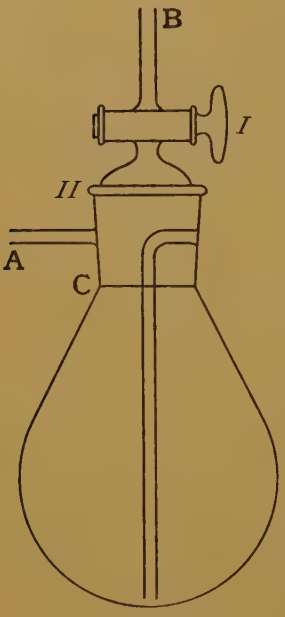

FIG. 3.

When the stop-cock *I* is open, a way is provided for a gas to pass from the flask through the hollow stopper *II* and out by the tube **B**.

The flask is of about 200 to 250 c.c. capacity, and a similar flask is provided of about the same weight and volume, to serve as a counterpoise in weighing. About the same amount of moisture will collect on the flask and on the counterpoise.

Place the flask in the thermostat and immerse up to **C** during the exhausting and filling.

1. Close *II*; open *I*; exhaust.

Close *I* and weigh. *Let weight* $= w_1$.

Repeat until the weight is constant.

2. Partially open *II*, allowing air to enter slowly. Repeat exhausting and filling.

Leave *II* open for 5 minutes. Close *II*, dry outside. Remove the calcium chloride tube and weigh. *Let weight* $= w_2$.

3. Connect the calcium chloride tube with a Kipp's carbon dioxide generator and fill with carbon dioxide, exhausting and filling twice as above.

Leave *II* open for 5 minutes in connection with the gas generator. Close *II* and disconnect from the generator, and remove the calcium chloride tube.

Slowly open *II*, and immediately close so that the pressure in the flask may equal atmospheric pressure. Dry and weigh. *Let weight* $= w_3$.

Then $$\frac{\text{density of carbon dioxide}}{\text{density of air}} = \frac{w_3 - w_1}{w_2 - w_1}.$$

If the density of air $= 14{\cdot}4$, calculate the density of carbon dioxide. The allowable error of this experiment is less than 1 %.

Note that the flask contracts when the internal pressure is removed. Therefore the bulb displaces less air when empty than when filled; so that there should be added to the observed weight of each gas an amount equal to the weight of the air displaced by the full bulb in excess of that displaced by the empty one. Through not correcting for this source of error, Regnault obtained the density of oxygen about 0·3 % too high.

Note also that if the pressure and temperature of the air displaced changes in the interval between the weighing of the empty flask and the weighing of the flask filled with gas, then the error in the small weight of the gas may be a large fraction of that weight. The use of a counterpoise, however, serves to reduce this error.

EXERCISE 2.

Determination of Density of Carbon Dioxide by Graham-Bunsen Effusion Method.

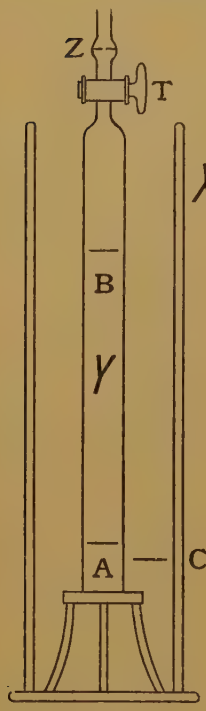

FIG. 4.

Fill cylinder *X* with water (see Fig. 4). Shut **T**. Place *Y* containing air (along with its stand) inside *X*, open **T** and allow air to **effuse** through the small hole in the thin platinum plate **Z**.

Observe the height of the water in *X*, when the level in *Y* rises to **C**, and add enough water in all the experiments to have the same head of water. Also, as the level in *Y* rises, note the times when it reaches the marks **A** and **B**. Repeat several times; let the time from **A** to **B** be t_1.

Fill *Y* with water to **T**, place in *X* and fill *Y* with carbon dioxide, and proceed as with air, always taking care to have the same head of water as before. Let the time for carbon dioxide be t_2.

Then

$$\frac{\text{density of carbon dioxide}}{\text{density of air}} = \frac{(\text{velocity of effusion of air})^2}{(\text{velocity of effusion of carbon dioxide})^2} = \frac{t_2^2}{t_1^2},$$

or density of carbon dioxide $= \frac{t_2^2}{t_1^2} \times 14{\cdot}4$.

The allowable error is less than $\pm 1\%$.

After this experiment the stop-cock should be closed, and then a plug of cotton wool should be placed in the mouth of the tube above the small hole. This prevents dust and moisture from entering and altering the size of the hole.

EXERCISE 3.

Determination of Vapour Density: Victor Meyer's Method.

Blow out any vapour that may be in the tube **B** (see Fig. 5), by means of a bellows. Then place the apparatus as in the figure, with the exception of **F**, which is put into position later.

Place water and porous tile in the copper tube **A**, and put some asbestos in the bottom of **B**.

Heat the water to boiling, and continue heating until no more air-bubbles are driven off at the end of **D** in the water trough **E**.

While the heating is going on, weigh in a small stoppered bottle a quantity of chloroform. To fill the bottle use a capillary tube.

When the air in **B** has been heated long enough, fill the graduated tube **F** with water, invert and place in the position indicated in the figure.

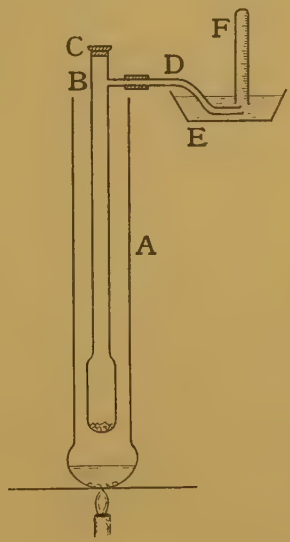

FIG. 5.

Quickly remove the cork **C**, slacken the stopper of the small bottle, drop in the small bottle containing the chloroform and replace the cork **C**. The volatile liquid is vaporised, and its vapour drives air out from **B** along **D** into **F**. When no more bubbles pass up **F**, remove **D** from the trough **E**, place the tube **F** in a large jar containing water, and after the temperature has become constant, measure the volume of *air + water vapour* in **F** at the temperature of the water in the jar and the pressure of the atmosphere. Find the pressure due to the air in **F** by subtracting the vapour pressure of water

from the barometer pressure, and calculate the volume of the air for 0° C. and 760 mm. pressure. Then calculate what weight of chloroform vapour would occupy 11·21 litres. (11·21 is rounded off from 11·206.)

The allowable error is less than ±5%.

In the Walker-Lumsden method, which is said to give good results, the volume is kept constant and the change in pressure is measured.

EXERCISE 4.

Determination of the Density of a Liquid by a Westphal Balance.

Test the setting of the balance. At first do not use any liquid, but on **S** (see Fig. 6) suspend the float **F**, allowing it

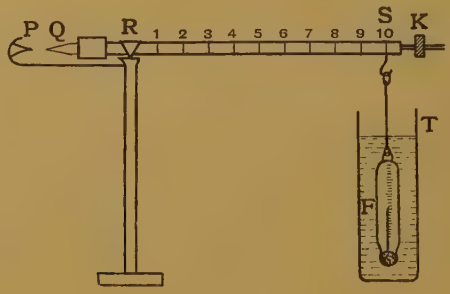

Fig. 6.

to swing freely in the air. If necessary, turn the screw **K** until the points **P** and **Q** are exactly opposite. Pour water into the jar **T**, and in the water immerse **F**, still allowing it to hang from **S**. **Q** has now fallen, and to bring it back to the position opposite **P**, a weight must be hung on the graduated beam to counteract the water's upward thrust.

Four weights of different sizes are provided:

$$A, \quad B\left(=\frac{A}{10}\right), \quad C\left(=\frac{A}{100}\right), \quad D\left(=\frac{A}{1000}\right).$$

For densities less than 1, only one of the size *A* is required. For densities greater than 1 and less than 2, two weights of the size *A* are required.

Now, if the water is at 4° C., the weight *A* placed at **S** should bring **Q** opposite **P** if the balance is going to give densities relative to water at 4°.

If the water is at 15° C., then, by placing *A*, *B* and *C* at 9 and *D* at 1, **Q** should be brought opposite to **P**, the balance reading being 0·9991, which is the density of water at 15°. If this reading cannot be obtained, it may be because the proper amount of water has not been used.

If this is the reading obtained with water at 15°, then for any other liquid at 15°, we obtain $D_{4^\circ}^{15^\circ}$, *i.e.* the density of the liquid at 15° relative to water at 4°. This assumes that the volume of the glass float does not change with change of temperature. Thus an error is introduced which would be got rid of by using fused quartz instead of glass.

To find the density of a liquid when the balance is set in this way, pour liquid into **T**, so that the level of the surface stands at the same place as in the case of water. If the temperature is 17° (say), and for equilibrium one of the two weights of size *A* is at 10 and the other at 5, also *B* at 3, *C* at 7, and *D* at 3; then the reading is 1·5373, or 1·5373 is $D_{4^\circ}^{17^\circ}$ for the liquid examined.

(If an instrument is used which gives a balance with water at 15° when *A* is at 10, then the reading with any liquid at, say, t° is $D_{15^\circ}^{t^\circ}$, *i.e.* the density at t° relative to water at 15°.)

Exercises: (I) If t° is the room temperature, determine $D_{4^\circ}^{t^\circ}$ for absolute alcohol.

(II) Calculate the molecular volume of alcohol, and compare the result with the sum of the atomic volumes given by Kopp for the B.P.

The error in the density as found by this method is sometimes put as being ±0·0005, but with care a much greater accuracy can be obtained.

Note that in work with this balance the same volume of liquid must be adhered to whatever the nature of the liquid. The float should be completely immersed in the liquid when enough has been added. Sometimes, in checking the instrument with water, a correct balance will not be obtained, because the proper quantity of water has not been used.

EXERCISE 5.

Determination of Vapour Pressure of a Solution by Dew-Point Method.

The apparatus used is a slightly modified form of that described by Cumming (*Jour. Chem. Soc.*, 1909, 95, 1772).

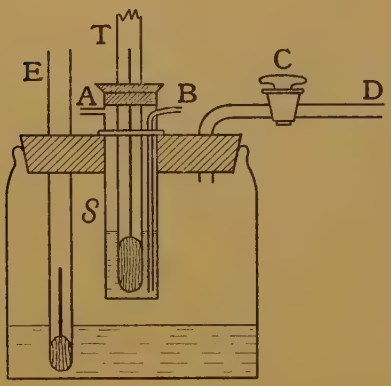

FIG. 7.

A wide-mouthed glass bottle is fitted with a rubber bung, through which pass a thermometer **E** graduated in tenths of a degree, a bent tube with a tap **C** (see Fig. 7), and a silver cylinder *S* highly polished on the outside, and having an outlet tube **A**, and an inlet tube **B** which reaches nearly to the foot of the cylinder. It is convenient to have these tubes made of silver and soldered into the cylinder. The cylinder is also fitted with an ordinary cork and a thermometer **T** graduated to tenths of a degree. Dissolve about 30·05 grams of urea ($\frac{1}{2}$ gram mol.) in 100 grams of water, and place some of the solution in the bottle, fit the bung, the bent tube, and the silver cylinder and thermometer. Connect **D** with a water pump and evacuate. Then close **C** and place the bottle in a thermostat at, say, 25°. When the temperature has had time

to steady, place some ether in *S*, and attach **A** to an aspirator, gently bubbling air in by **B** through the ether. The reading on **T** falls, and when it reaches a certain value, dew appears on the polished surface of *S*. Note this reading, and allow the temperature to rise again, and note the reading at which the dew disappears again. These readings should not differ by more than 0·2°. The mean between these two readings is the figure taken. Let this be $t°$. From Table II. obtain the vapour pressure of pure water at $t°$; this pressure is the vapour pressure of the given urea solution at 25°, and is lower than the vapour pressure of water at 25°.

Hence calculate the molecular weight of urea in the given aqueous solution, or the "**dissolecule**" of urea, using the formula

$$\frac{\pi_A}{p_A} = \frac{n_A}{n_A + n_B} \quad \text{or} \quad \frac{p_A - \pi_A}{p_A} = \frac{n_B}{n_A + n_B},$$

where π_A = vapour pressure of solution,
p_A = " " pure solvent,
n_A = number of mols. of solvent in the solution,
n_B = " " solute in the solution.

EXERCISE 6.

Determination of Vapour Pressure by the Isoteniscope Method.

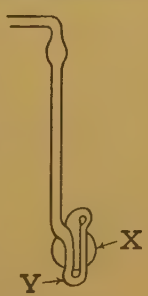

FIG. 8.

The **Isoteniscope** (see Fig. 8) consists of a long tube, at the end of which a bulb **X** is blown to hold the liquid, and a portion of which is bent into a U-shape **Y** to hold the same liquid and serve as a manometer.

The apparatus used in this experiment is shown in Fig. 9, and consists of a water pump **P**, a filter bottle **F** used as a trap, a mercury manometer **M** and the isoteniscope **I** placed in a beaker **Z** containing water, in which is placed a thermometer **T** and a stirrer **S**. For higher pressures,

about 1 atmosphere (say), a much longer mercury manometer must be used. **P**, **F**, **M** and **I** are connected with pressure rubber tubing, as shown in Fig. 9, in such a way that the

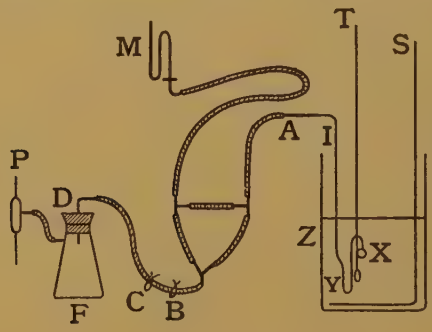

FIG. 9.

mercury in **M** and the liquid in **Y** are at the same distance from **P**. On the rubber tubing connected with **F** are fixed two screw clips **C** and **B**.

Determination of the Boiling Point of Benzene.

Place pure benzene in the isoteniscope so as to $\frac{1}{2}$ fill **X** and $\frac{1}{3}$ fill **Y**. Pour water at about 82° into **Z**, and place the isoteniscope in the water bath, not connecting at **A** at present. Keep stirring the water to maintain a uniform temperature throughout the bath. The benzene boils, and air and dissolved gases are driven from **X**. Allow the temperature to fall, stirring steadily. Note the temperature at which the level on both sides of **Y** is the same. At the same time read the barometric pressure. The observed temperature is the boiling point of benzene at the observed pressure. Calculate the boiling point of benzene for a pressure of 760 mm. from the formula

$$\log_e p_2 - \log_e p_1 = -\frac{L}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

or

$$\log_{10} p_2 - \log_{10} p_1 = -\frac{0{\cdot}4343L}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right),$$

where L = latent heat for 1 gram mol. and $R = 2$ (approx.),

T = absolute temperature and p = corresponding pressure in mm.

Determination of the Vapour Pressure of Benzene for Various Temperatures.

Boil the benzene as in the last experiment for some time to expel air and gases. Then connect the apparatus as in Fig. 9, using a long mercury manometer and leaving **F** disconnected at **D**. Open **C** and **B** and the manometer. By means of a bicycle pump connected at **D**, raise the pressure above 1 atmosphere. Shut **B** tight and disconnect the bicycle pump. Heat the bath until the benzene boils. In **Y** there is a higher level on the side remote from **X**. Stop heating, but keep stirring the bath, and allow the isoteniscope to cool until in **Y**, a slightly higher level is on the side nearer **X**. Shut **C** tight and open **B**. This allows the small portion of air between **C** and **B** to mix with the air and vapour in the apparatus, and thus the pressure is reduced. If the levels in **Y** are still different, shut **B** tight, open **C**, shut **C** tight, open **B**. This reduces the pressure still further. Repeat until the levels in **Y** are the same, when the reading on the manometer gives the vapour pressure of benzene for the temperature of the bath.

For pressures lower than 1 atmosphere connect with the water pump as in Fig. 9, still using the long mercury manometer. Open the screw clips **C** and **B**, and the mercury manometer. Allow the temperature of the bath to fall slightly. This fall may be accelerated by adding cold water and stirring. Start the pump **P**, and continue pumping until the benzene boils. Allow to boil for some time to drive out the air from **X**. Shut **B** tight, disconnect at **D** by pulling the glass tube out from the rubber stopper. Stop the pump. In **F** there is a higher level on the side remote from **X**. Shut **C** tight and open **B**. This allows the small portion of air between **C** and

B to enter the apparatus. If the levels in **Y** are still different, shut **B** tight, open **C**, shut **C** tight, open **B**. This allows another small portion of air to enter. Repeat until the levels in **Y** are the same, when the reading on the mercury manometer **M** gives the vapour pressure of benzene for the temperature of the bath.

Repeat for lower temperatures by cooling the water slightly. For ordinary temperatures the short manometer shown in the figure may be used.

For the isoteniscope, see A. Smith, *Jour. Am. Chem. Soc.*, 1910, etc.

FIG. 10.

EXERCISE 7.

The Beckmann Thermometer.

The Beckmann thermometer (see Fig. 10) has a large bulb at the foot, a very narrow bored stem, and at the top a reservoir of mercury.

The large bulb can have its supply of mercury increased or diminished by taking mercury from or giving up mercury to the reservoir.

The Beckmann thermometer may thus be set for various ranges of temperature, each range usually extending to 5 or 6 degrees (sometimes to 1 or 2 degrees). Each degree is usually divided in tenths and hundredths of a degree.

The setting of any particular instrument should be restricted to ranges of temperature in a limited portion of the temperature scale. For example, one instrument should be reserved for freezing-point experiments in the neighbourhood of 0° C., and another for boiling-point experiments in the neighbourhood of 100° C.

Setting of Beckmann Thermometer.

In a Beckmann having a range of about 6 degrees for experiments in which a rise above (say) 15° has to be measured, set the instrument so that the mercury in the capillary stands

at a point about 1 degree from the foot of the range, when the bulb is placed in a liquid at 15°. To do this, place the bulb in a bath at about 22°, *i.e.* about 7° above 15°; then there are three possibilities:

(1) The mercury may rise to exactly fill the capillary part. In this case, when the thermometer is placed in the 15° bath, the mercury will fall to the proper place, about 1 degree from the foot of the range.

(2) The mercury may rise to more than fill the capillary part. In this case, quickly take the thermometer from the bath, hold the instrument upright and jerk the excess of mercury down into the reserve in the top reservoir. If this has been done before the mercury has begun to contract, the instrument will be found to be properly set; if not, the heating and jerking must be repeated.

(3) The mercury may rise to less than fill the capillary part. In this case, invert the thermometer and jerk some mercury from the reservoir to fill the little bend where the reservoir bulb joins the long capillary. Change back to the regular upright position adopted in measuring temperature. Some mercury is now found to be retained in the top bend. We can see in this way how much mercury we are about to add. If the amount seems too large, jerk the excess down into the reservoir. Thus the mercury caught at the top can be reduced to the small amount just sufficient to fill the little capillary bend. Place the thermometer in a bath at a higher temperature than 22°, so that the mercury below rises to join the trapped mercury at the top. Allow to cool to 15°. If necessary, repeat the above, adding mercury in very small increments until the required setting is obtained.

For experiments in which a fall below 15° has to be measured, set the instrument so that the mercury in the capillary stands at a point about 1 degree from the top of the range. In this case, use a bath at about 18°, *i.e.* about 3° above 15°, and proceed as above.

24 hours should elapse between the setting and the using of the Beckmann, to allow for lag of the glass.

As an exercise, set the thermometer for use in measuring a rise above Room Temperature.

Effect of Pressure.

To show the effect of pressure on the glass, place the Beckmann in a rubber cork fitted into a thick-walled filter-bottle. Observe the position of the mercury on the thermometer scale. Evacuate the bottle, and observe that the mercury has fallen in the capillary owing to the expansion of the bulb arising from the reduced pressure. Therefore, a correction must be introduced in determination of boiling points under reduced pressure, and in other temperature determinations in which a pressure other than the ordinary is employed.

Compare in this connection the correction which must be introduced in accurate determinations of densities of gases by Regnault's weighing method.

Correction to be made when the Amount of Mercury in the Bulb of a Beckmann is reduced.

Let the Beckmann be made of Jena normal glass (16'''), and suppose that it reads 0° at 0° C. and 1° at 1° C. Then the small amount of mercury filling the bore of the capillary from 0° to 1° is equal to $\frac{1}{6370}$ of the total volume of mercury at 0° C. Take this small volume as unit volume ; then the volume at 0° is 6370.

Now, suppose that there is transferred to the top reservoir enough mercury to fill 10 degrees of the bore of the capillary. The temperature is now 10° C. when the Beckmann reads 0°. If the temperature is raised to 11° C., the apparent increase in volume of mercury is $\frac{1}{6370} \times (6370 - 10)$ or $1 - \frac{10}{6370}$,

i.e. the Beckmann reads less than 1° by $\frac{10}{6370}$,

or $(1 - \frac{10}{6370})$ of a Beckmann degree $\equiv$ 1 degree Centigrade,

or 1 Beckmann degree $\equiv \frac{6370}{6370 - 10}$ of a degree Centigrade

$\equiv 1{\cdot}0016°$ C.

EXERCISE 8.

Raising of Boiling Point: Landsberger-Walker Method.

Apparatus: **F** is a boiling flask (see Fig. 11) in which is placed some of the pure solvent. Of ordinary solvents the best are alcohol and ether. **G** is a graduated tube surrounded by a wider tube connected with a condenser.

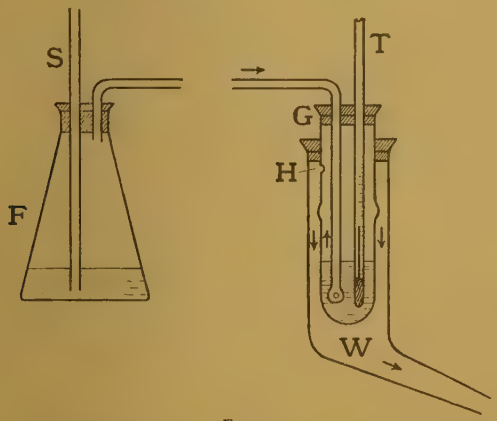

FIG. 11.

T is a thermometer graduated in tenths of a degree.

S is a safety tube which should extend a foot above the cork.

Calibrate **G**. Run water from a calibrated burette into **G**. Take readings on the burette scale corresponding to readings on **G** scale. Fit the apparatus as in Fig. 11. Place some pure solvent with porous tile in **F**, also 10 to 12 c.c. in **G**. Heat **F**, allowing vapour of the solvent to bubble into the liquid in **G**. Some condenses there, the remainder passes up **G**, out by **H**, down **W** to the condenser, from the end of which a regular succession of drops should fall, say one a second or one every 2 seconds. When the temperature is steady take a reading for the boiling point of the pure solvent (alcohol). Remove most of solvent from **G**, leave about 5 c.c. To this add a

weighed quantity of benzoic acid (0·20 gram), best in the form of a tabloid (see page 51). Place fresh tiles in **F**. Pass vapour again, so that the same number of drops is obtained as before. Take the temperature of boiling. Immediately remove **G** and take the volume of the solution.

Place fresh porous tile in **F**. Pass vapour, taking the B.P. and the volume for the second time.

Place fresh porous tile in **F**. Boil again, taking B.P. and volume for the third time.

Three boiling points with corresponding volumes will thus be got.

In the following:

Solvent.	K.	Latent Heat of Vaporisation.	Δt.
Water - -	5·4	535·9	0·0376
Ethyl alcohol -	15·6	215·0	0·0340
Ether - -	30·3	90·0	0·0398
Acetone - -	22·2	125·3	0·030

K is the elevation of the B.P. obtained when a gram molecule of solute is dissolved in 100 c.c. of solvent, and Δt is the change in the B.P. for a change of 1 mm. in the atmospheric pressure.

(1) Calculate x, the weight of solute in 100 c.c.

(2) Calculate M, the molecular weight of benzoic acid in the alcoholic solution at its B.P. or the "**dissolecule**" of benzoic acid, from

$$\frac{M}{x} = \frac{K}{e}$$ (e = elevation obtained in the experiment).

Note the influence of change of atmospheric pressure on the B.P. and introduce a correction if necessary.

The allowable error of this method is 5 to 10%, but this accuracy is sufficient for the determination of molecular weight from a knowledge of the empirical formula.

Tabloid Press.

To obtain a powder in the form of a short rod or tabloid, use the apparatus shown in Figs. 12, 13 and 14, which consists of a mould **M**, stopper **S**, collar **C** and plunger **P**, and also a press, all made of steel. Clean the mould **M** (see Fig. 12),

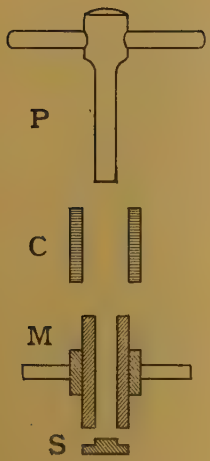

Fig. 12.

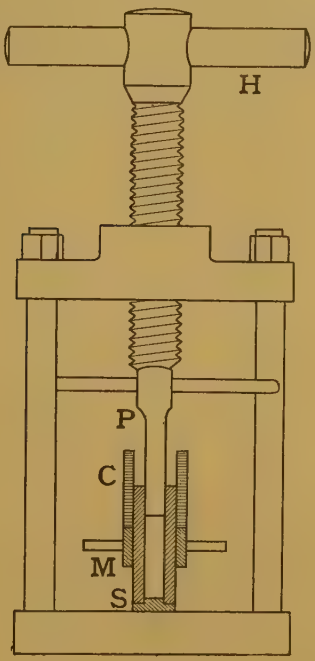

Fig. 13.

especially the circular bore in which the tabloid is to be formed. Also clean the stopper **S**, the collar **C** and the plunger **P**. Close the mould **M** at the foot with the stopper **S**, and place the collar **C** round the top of the mould **M**. Inside the collar place some of the powder, and by means of **P** push the powder into the bore of **M**. Leaving the plunger **P** in position in the

bore of **M**, transfer the whole to the press (see Fig. 13). Turn the handle **H** of the screw, and thus force the plunger **P** down the bore of the mould **M**, and in this way press the powder into one coherent mass. To extract the tabloid, remove the mould from the press, take out the stopper **S** and the plunger **P**. Place **S** in the recess in the foot of the press. Transfer the collar **C** from above to below the mould **M** (see Fig. 14), and push the lower end of the mould into **C**. Put the plunger **P** into the bore of the mould, and place the whole in the press again. Turning the screw, force the tabloid out from the mould.

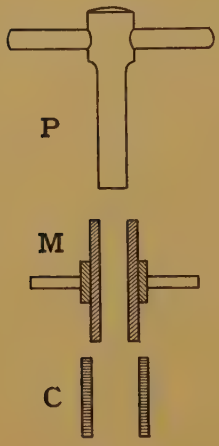

FIG. 14.

Before laying aside the apparatus, clean out all the powder, using a solvent. Then thoroughly smear with vaseline to prevent corrosion.

EXERCISE 9.

Raising of Boiling Point (Beckmann's Method).

For very accurate determinations, it is essential to obtain a constant boiling point. Fluctuations in the thermometer reading are due not only to causes within the boiling liquid (ebullition which is not uniform throughout the liquid, and unsteady ebullition) but also to causes outside the boiling liquid (irregular radiation, currents of hot gases from the heating flame, and an irregular supply of heat).

Non-uniform ebullition. This leads to irregular stirring and local superheating. Uniform bubbling is obtained by placing in the boiling tube a layer of garnets or glass beads or "platinum tetrahedra," which replace the larger bubbles by

smaller ones which are regularly distributed throughout the liquid. The beads should be added until further addition produces no appreciable change in the B.P. With the usual size of boiling tube a layer of 3 or 4 cms. may be required. It is possible to add too many beads, which trap portions of the liquid so that irregular stirring is again obtained.

Unsteady ebullition. If this is very marked we have *boiling with bumping*, so troublesome in gas-free liquids. This may be avoided by placing in the liquid some porous material, in the pores of which is air which acts as a nucleus round which vapour bubbles can form. Pieces of porous porcelain, for example, act in this way, or "platinum tetrahedra."

When the boiling has once started it goes on steadily. But if the boiling is stopped, on heating again we find that the porous material has now lost its power of starting steady boiling, and fresh material must be added. The platinum tetrahedra should be added until further addition produces no appreciable change in the B.P. Between 20 and 30 tetrahedra may be required, and if these are used no beads need be added, and the boiling tube need not be so large as would otherwise be necessary.

Irregular radiation. This is overcome by reducing the radiation to a minimum by surrounding the boiling tube with a jacket containing solvent kept at the B.P.

Current of hot gases. To prevent hot gases from coming in contact with the boiling tube and causing superheating, the space between the boiling tube and the mantle is packed with asbestos.

Irregular supply of heat. This is avoided by protecting the flame from draughts and keeping the supply of gas as regular as possible. The flame should be gradually raised until further raising produces no appreciable change in the B.P. The electrical method of heating, however, is the best; a fine resistance wire of platinum is used, and a regular supply of heat is obtained by keeping the current constant.

Exercise in Beckmann's Method. Close with corks and weigh the empty boiling tube **B** (see Fig. 15). Add about 20 c.c. of benzene, cork and weigh again.

Add a sufficient supply of clean, dry, platinum tetrahedra or garnets or glass beads, and place a Beckmann thermometer in the boiling tube **B**, so that its bulb is covered with the benzene and stands a little above the beads or tetrahedra.

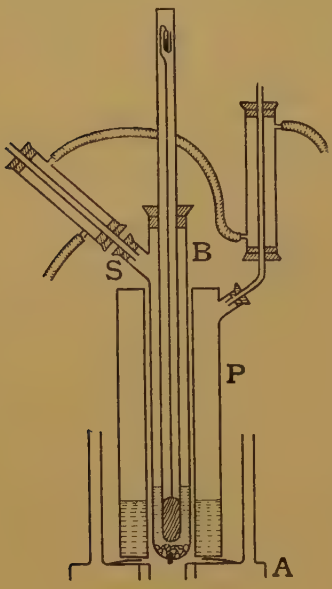

Fig. 15.

Put **B** in position in the apparatus inside the porcelain jacket **P**, in which place some benzene and small pieces of porous tile. Fit some asbestos paper between **B** and **P**. Connect, in series, a reflux condenser to **P**, and one to the side-tube **S** of **B**. Heat with a ring burner or a single burner for **P**, and single burner for **B**, placing the burners under the asbestos box **A**, provided with chimneys for conveying hot air past the apparatus.

Protect the flames from draughts, and boil briskly. A platinum wire passing through the foot of **B** helps to render the boiling steady. Note the number of drops of benzene refluxing from the condenser per minute, and see that the boiling is at the same rate in the second half of the experiment. When the temperature reading on the Beckmann has remained constant for about 5 minutes, take the thermometer reading, and at the same time note the atmospheric pressure, put out the burners, and when the boiling has stopped, remove the reflux condenser from **S**, and through **S** drop into **B** about

·3 gram of ethyl benzoate (accurately weighed), using a pipette similar to **Z** (Fig. 17).

Replace the reflux condenser in **S**, and heat again as before until the Beckmann shows a constant temperature. Take this reading, and at the same time note the atmospheric pressure.

Before taking a thermometer reading, tap the thermometer with the finger to prevent the mercury thread from sticking in the stem.

If the second atmospheric pressure is not equal to the first, then the first B.P. (that of pure solvent) must be altered to a figure corresponding with the second atmospheric pressure.

In the following:

Solvent.	Boiling Point.	t_m.	Latent Heat of Vaporisation.	Δt.
Water - -	100°	5·2	535·9	0·0376
Ethyl alcohol	78°·4	11·5	215·0	0·0340
Ether - -	34°·6	21·0	90·0	0·0398
Acetone -	56°·1	17·0	125·3	0·030
Benzene -	80°·2	27·0	92·9	0·043

t_m is the elevation of the B.P. obtained when a gram molecule of solute is dissolved in 100 grams of solvent and Δt is the change in the B.P. for a change of 1 mm. in the atmospheric pressure.

In the above experiment:

(1) Calculate x, the weight of ethyl benzoate in 100 grams of benzene.

(2) Calculate M, the molecular weight of ethyl benzoate in the benzene solution at its boiling point, or the "**dissolecule**" of ethyl benzoate, from

$$\frac{M}{x} = \frac{t_m}{e},$$

where e = elevation of B.P. obtained in the experiment.

Note that $K \times s = t_m$,

where K = constant used in Landsberger Method, and s = density of solvent at B.P.

The allowable error of this method is about 3 %.

In a simpler form of apparatus, instead of the liquid mantle **P** there are used two concentric glass cylinders which are supported in the centre of a board of asbestos. A circular hole in the centre of the board is covered with a small piece of wire gauze, and is directly under the boiling tube **B**, which is heated by means of a small flame placed under the wire gauze and protected from draughts by a mica funnel. Asbestos is packed, at the top end, between the two cylinders and between the inner cylinder and **B**. In addition it is well to have a sheet of mica resting on the top of the glass cylinders. This protects the upper part of the apparatus from hot-air currents. **B** is provided with a reflux condenser, and the experiment is carried out as with the more complicated apparatus.

EXERCISE 10.

Raising of Boiling Point (Electrical Heating).

If **electrical heating** is adopted, the apparatus becomes very simple (see Fig. 15*a*). The boiling tube **B** has a reflux condenser **C** fitted to its side tube **S** as before, is provided with a Beckmann and is supported in a Dewar flask **D**, which acts as a heat mantle. Two stout copper or nickel or platinum wires **W, W** pass down through the thermometer cork, and the lower ends of the wires are connected with a spiral of platinum wire about 0·25 mm. in diameter, which serves as a heater. To improve the steadiness of the boiling, it is well to have the platinum spiral freshly platinised, the wire being raised to a dull red heat after the deposition. The thermo-

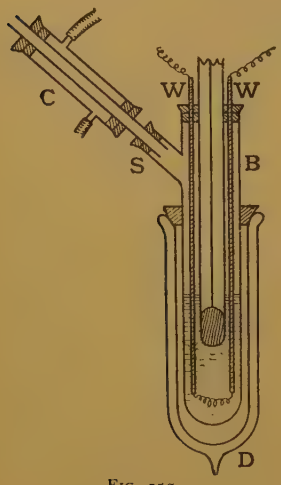

FIG. 15*a*.

meter bulb should be placed under the surface of the liquid and as far above the spiral as possible. Copper as a material for the wires **W**, **W** is of only limited application, nickel is more generally applicable, but platinum is to be preferred. The wires must be fairly stout, thus an objection may be raised to the use of platinum. For the wires **W**, **W**, however, there may be substituted glass tubes closed at the lower ends, through which are fused short stout pieces of platinum wire to which the resistance spiral is attached by welding or by the use of gold solder. Inside the glass tubes is put a little mercury, through which connection is made to the accumulators.

Using glass tubes instead of **W**, **W**, determine the raising of the B.P. when ·5 gram of camphor is dissolved in about 17 grams of benzene. Use accumulators as a source of current, and put a regulating resistance and an ammeter in the circuit. To obtain a steady supply of heat it will be necessary to keep the current constant. The current required will depend on the nature of the solvent and the dimensions of the heating wire and of the apparatus. With 17 grams of benzene and a heating wire having a diameter of 0·25 mm. and having a resistance of 0·3 ohm, it will be found convenient to use 3 accumulators, and to pass a current of 5 ampères through the circuit.

EXERCISE 11.

Lowering of Freezing Point.

Dry, close with unbored corks and weigh the freezing tube **F**. Into **F** weigh about 20 grams of glacial acetic acid. In jar **J** (see Fig. 16) place water, a thermometer **T** and a stirrer **Y**, add ice to obtain on stirring a cooling bath of about 14° C. (3° below the F.P. of acetic acid). Through the central hole in the cover **C** of the jar **J**, push the inner tube **I** (dry inside). Inside **I** place **F**. In **F**, place Beckmann thermometer **B** so

that the bulb is covered by the acetic acid; also in **F** place platinum stirrer **X**. **B** and **X** pass through a double bored cork placed in the mouth of **F**. In the bore, through which **X** passes, is placed a narrow glass tube to facilitate the working of **X**. It will also be found an advantage to have a glass tube round the upper portion of **X**. The side tube of **F** is closed by an unbored cork.

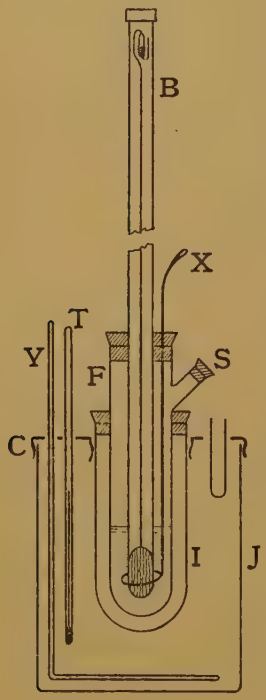

FIG. 16.

Remove **F** from **I**, push **F** through the hole in **C** so as to immerse **F** directly in the cooling bath. Stir slowly with **Y** and vigorously with **X** until freezing commences in **F**. Quickly remove **F** from bath, dry the outside of **F** and place **F** in **I**. Stir regularly with **X**. The temperature reading on **B** is increasing in the meantime. Take the maximum reading, tapping the thermometer before each observation. An approximate freezing point is thus obtained.

Remove **F** from **I**, melt the acid with heat from the hand and place **F** again directly in the cooling bath, but now stir slowly with **X** and allow the temperature to fall only about $0°{\cdot}5$ below the approximate F.P. This small amount of super-cooling may not start freezing. Remove **F** quickly, dry the outside of **F** and the inside of **I**, place **F** in **I** and stir vigorously with **X**. A rapid rise in the Beckmann reading shows when the freezing has commenced; then stir slowly with **X** and note the maximum temperature. Repeat, taking at least 3 readings, which should be concordant. Use the mean for calculations.

If the cooling of **F** when in the bath is rapid, it is advisable to remove **F** to **I** even before the approximate F.P. is reached, and to allow the final cooling to take place in **I**.

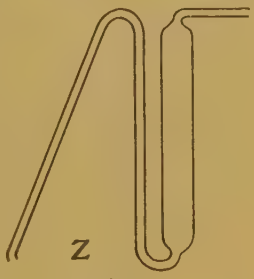

FIG 17.

Through the side tube **S**, blow into **F**, by means of the pipette **Z** (Fig. 17), 0·3 gram of acetone, the weight being obtained by difference. (Blow some acetone into a beaker, first, to form an idea of the bulk of 0·3 gram.) Determine the F.P. as before; a lower figure is now obtained. Note the depression of the freezing point.

In the following:

Solvent.	Freezing Point.	t_m.	Latent Heat of Fusion.
Water - -	0°	18·6	79·1
Acetic acid -	17°	39·0	43·1
Benzene -	5°·5	50·0	30·1

t_m is the depression of the F.P. obtained when a gram molecule of solute is dissolved in 100 grams of solvent.

In the above experiment:

(1) Calculate x, the weight of acetone in 100 grams of acetic acid.

(2) Calculate M, the molecular weight of acetone in the acetic acid solution at its F.P. or the "**dissolecule**" of acetone, from

$$\frac{M}{x} = \frac{t_m}{d},$$

where d = depression of F.P. obtained in the experiment.

The allowable error is about ± 5 %.

In the case of a hygroscopic solvent such as acetic acid, for great accuracy, care should be taken to exclude moisture by a modification of the experimental details given here.

EXERCISE 12.

Determination of Transition Point (Thermometric Method).

Take as an example the transformation:

$$Na_2SO_4 . 10H_2O \rightarrow Na_2SO_4 + 10H_2O.$$

In a boiling tube, place about 30 grams of pure sodium sulphate decahydrate. Hang a thermometer, graduated in tenths of a degree, with its bulb completely surrounded by the decahydrate. Immerse the boiling tube in a water bath contained in a large beaker heated with a small flame. Keep the temperature of the water-bath uniform by means of a stirrer. Raise the temperature of the bath to about 31°, then keep the temperature constant. Now slowly raise the temperature until the salt becomes partially liquid. Stirring both the salt and the bath, raise the temperature at the rate of about 1° in 10 minutes. Plot times as ordinates against the temperature (see Fig. 18). A point is reached at which the temperature is practically constant for an interval. This is due to absorption of heat during the transition from decahydrate to anhydrous salt and solution. After a time, the temperature rises regularly again. This irregularity occurs about 32° to 33°.

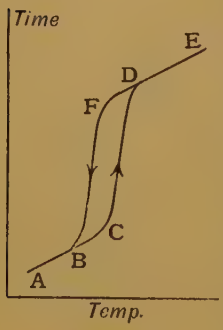

FIG. 18.

When the temperature has reached 35°, allow to cool, stirring both salt and bath, and plot a temperature-time curve as before. An irregularity or break in the curve will be found as before, but owing to **suspended transformation** the perpendicular portion of the cooling curve may not coincide with the perpendicular portion of the heating curve.

The appearance of the time-temperature curve is seen in

Fig. 18. **ABCDE** is the heating curve, **CD** corresponding to **transition**, whilst **EDFBA** is the cooling curve, **FB** corresponding to transition.

DETERMINATION OF TRANSITION POINT

(Dilatometric Method).

When a substance passes from one form to another there is usually a marked change in its properties. Thus, if the temperature of a substance is gradually raised, there will be a gradual variation of its properties until the transition point is reached, at which an abrupt change will be observed. Study the transition :

$$Na_2SO_4 . 10H_2O + MgSO_4 . 7H_2O \rightarrow MgSO_4 . Na_2SO_4 . 4H_2O + 13H_2O.$$

When the transition is complete, the variation of properties with temperature again becomes gradual. This phenomenon is made use of in determining the **Transition Point.** For example, the variation of volume with temperature may be studied. The instrument used is called a **dilatometer.** This consists of a long capillary tube **A**, of about 0·5 mm. internal diameter, which widens out into a long bulb at the end after the manner of a thermometer. The bulb is also open at the other end **C** (see Fig. 19). To use the dilatometer, invert it, drop in a glass bead to close the end of the capillary, and prevent solid from entering the capillary. Take equimolecular weights of sodium sulphate decahydrate and magnesium sulphate heptahydrate. Having powdered each, mix them, using only a glass rod. Place some of the mixture in the bulb to fill about three-quarters. Fuse off the open end **C**, allow to cool and invert back to the proper position, shaking down the solid. By means of a

Fig. 19.

rubber stopper, attach an adapter to the upper end of the capillary tube (see Fig. 20).

Place petroleum in the adapter, and connecting the adapter with a water pump, extract as much air as possible from the dilatometer. Disconnect the pump, when the petroleum will be forced into the dilatometer. Repeat the pumping until all the air has been removed. The surface of the petroleum should be at the lower end of the capillary, if the proper quantity has been forced in. If more than this amount has been added, the excess may be removed by pushing a very fine capillary tube down the capillary of the dilatometer, and connecting with the pump. Attach a scale to the capillary tube, so that the meniscus of the liquid is at the bottom of the scale. Place the bulb of the dilatometer in a beaker of water at about 16°, and allow the bulb time to acquire the temperature of the bath. Note the temperature and the position of the meniscus on the scale. Slowly raise the temperature so that in about 10 minutes it has risen 1°; then keep the temperature constant until the meniscus has ceased to rise. Take corresponding temperature and scale readings. Raise the temperature 1°, and note another pair of corresponding readings. Proceed in this way, degree by degree, until about 25° is reached. Plot the heights of the meniscus as ordinates against the temperature readings.

FIG. 20.

There will be found to be an abrupt increase of volume at a certain temperature between 21 and 22, which, owing to **suspended transformation**, is a little above the true transition temperature. Now allow the dilatometer to cool, and note corresponding pairs of readings as before, obtaining a cooling curve. An abrupt contraction is observed at a certain temperature, which is a little below the true transition temperature owing to suspended transformation. Thus the heating and cooling curves do not

coincide. From the two curves, deduce the true transition point.

Curves similar to those in Fig. 18 will be obtained.

When the time available for this experiment is limited the demonstrator may at the beginning of the course charge one dilatometer and have it fitted up ready for heating.

EXERCISE 13.

Distribution Factor.

Prepare 250 c.c. of $\frac{n}{20}$ sodium hydroxide.

(1) Into a stoppered bottle put 100 c.c. of ether and 100 c.c. of water, and add 1 gram of succinic acid.

Place in a thermostat at 25°, shaking occasionally until equilibrium is reached.

(2) Into another stoppered bottle put 100 c.c. of ether and 100 c.c. of water, and add 0·5 gram of succinic acid.

Place in the same thermostat, shaking occasionally until equilibrium is reached.

Titrate 25 c.c. of each layer of (1) with $\frac{n}{20}$ NaOH. Let the titration figure for the ether be x, and for the water y.

Titrate similarly for (2), and let the figure be for ether z, and for water w.

Then we should obtain $\frac{x}{y}=\frac{z}{w}$.

The above holds only when the **dissolecule** in the ether equals the **dissolecule** in the water layer. If the first dissolecule were the simple molecule and the second dissolecule equalled n simple molecules, then

$$\frac{x}{\sqrt[n]{y}}=\frac{z}{\sqrt[n]{w}}.$$

Allowable error is 3 to 5 %.

To verify the **Distribution Law** it is not necessary to know the exact strength of the sodium hydroxide solution.

EXERCISE 14.

Determination of the Relative Viscosity of Benzene.

When a liquid flows through a capillary tube, it arranges itself in tubes of liquid which slip past one another like the tubes of a telescope. The farther the liquid tubes are from the wall of the bore, the faster do they move relative to the wall. The tangential force **F** per unit area, required to make a liquid tube move with a velocity v relative to another tube at a distance y, is given by

$$F = \frac{\eta v}{y},$$

where η is the coefficient of viscosity.

FIG. 21.

What is usually measured in Physical Chemistry is the viscosity of a liquid relative to that of a standard liquid, for example, water.

The commonest apparatus (see Fig. 21) consists of a glass capillary tube **CD** about 0·25 to 0·4 mm. diameter and 10 to 12 cms. long. To the top of this tube is fused a wider tube blown into a bulb **X** at the foot and having a narrow part at **B**. To the foot of the capillary tube is fused another wide tube which is bent up to the same height as the other half of the vessel and is blown into a bulb at **E**. There is a mark etched on the glass above the bulb **X** at the point **B**, and another below at the point **C**.

Thoroughly clean the viscosity tube with warm sulphuric acid and potassium dichromate mixture. There should be no appearance of oiliness on the surface of the glass. Wash out with distilled water with the aid of the filter-pump, and dry the tube, by leading through it a current of air which has been filtered through cotton wool and heated. Place the viscosity

tube in a thermostat with transparent sides at 25°. Illumination of the bath with a small electric lamp hung over the side will facilitate the measurements.

Prepare some air-free distilled water. Introduce a definite volume, say 10 c.c., of distilled water at 25° into the wider limb of the viscosity tube. If the volume taken is suitable, the liquid should stand in the bulb **E** about half-way up. Attach a rubber tube to the narrow limb, and suck the water up until the meniscus stands about 2 cms. above the top etched mark. Allow the liquid to fall, and measure with a stop-watch the time taken by the meniscus to pass from the top-mark **B** to the lower mark **C**. Repeat several times and take the mean of the readings. If the tube is suitable for use with the given liquid, the time should be at least 100 seconds.

Dry the tube and carry out a measurement with benzene at 25°, using the same volume (10 c.c.). The coefficient of viscosity for benzene η_{benzene} is calculated from the formula,

$$\frac{\eta_{\text{benzene}}}{\eta_{\text{water}}} = \frac{\text{time for benzene} \times \text{density of benzene}}{\text{time for water} \times \text{density of water}}.$$

η for water at $25° = 8{\cdot}926 \times 10^{-3}$.

For the densities of benzene see Table VI. Allowable error is less than 1 %.

EXERCISE 15.

Surface Energy.

Surface Energy per square cm. of a liquid surface
= (numerically) Surface Tension per linear cm.
$= S$.

Let V = volume occupied by 1 gram molecule,

i.e. V is proportional to the volume per molecule,

and $V^{\frac{2}{3}}$ is proportional to the area per molecule.

$S \times V^{\frac{2}{3}}$ = surface energy calculated for a fixed number of molecules
= **molecular surface energy.**

Ramsay and Shields found $S \times V^{\frac{2}{3}}$ to be a linear function of T over a wide range.

At T_K (critical temperature) the surface tension between liquid and vapour vanishes, because above this temperature the substance does not exist in two distinct layers.

For a wide range of temperature, the relation

$$S \times V^{\frac{2}{3}} = K(T_K - T) \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

is nearly true, but near T_K the relation is not so simple. If S and V have the values S_1 and V_1 at the temperature T_1 and the values S_2 and V_2 at the temperature T_2, then

$$S_1 V_1^{\frac{2}{3}} = K(T_K - T_1),$$

$$S_2 V_2^{\frac{2}{3}} = K(T_K - T_2);$$

$$\therefore \; S_1 V_1^{\frac{2}{3}} - S_2 V_2^{\frac{2}{3}} = K(T_2 - T_1), \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where $K = 2{\cdot}12$ and V is calculated thus: If x single molecules unite to give 1 larger molecule, then xM = gram molecular weight obtained as the result of association, and the corresponding gram molecular volume $= xMv$, where M = mass of a single gram molecule and v = specific volume.

Method of Measurement.

Into a boiling tube is fitted a double bored rubber stopper through which passes a stout-walled capillary tube (of about 0·2 to 0·3 mm. diameter in bore) and a right-angled tube passing just through the stopper. To the capillary tube is attached a millimeter scale. The tube is adjustable to any height in the boiling tube.

Thoroughly clean out the boiling tube and the capillary with potassium dichromate and sulphuric acid mixture, and wash with distilled water, using a pump to draw the liquids through the capillary. Alcohol or ether should not be used as washing liquids. Finally dry the capillary by passing a current of hot air previously filtered through cotton wool.

Put benzene into the boiling tube and place the capillary in position. Fix the apparatus in a thermostat (at 25°) with transparent sides. Illumination of the bath with a small electric lamp hung over one side will facilitate the measurements.

Blowing in at the right-angled tube, force the benzene up the capillary and allow it to fall to the position of equilibrium. Take the difference of the level of the benzene inside and outside the capillary tube. Repeat several times.

Sucking at the right-angled tube, pull the benzene down the capillary and allow it to rise to the position of equilibrium. Repeat several times.

The different readings should not differ by more than ±0·2 mm., otherwise the capillary should be cleaned.

Using the formula $S = \frac{1}{2}hrsg$,

where S = surface tension,

h = height of liquid in capillary,

r = radius of capillary,

s = specific gravity of liquid,

g = 981 dynes,

and the values of S and s for benzene given in Table VI., calculate the radius of the tube.

Repeat the experiment at 50°, adjusting the position of the capillary tube so that the meniscus of the liquid is at the same point in the bore of the tube as in the experiments at 25°. Take the mean of the two results for the value of r.

Carry out similar experiments with water at 25° and 50°, and using the value of r obtained above, and the same formula as before, calculate the values of S at 25° and at 50°. Hence calculate x **the factor of association** of water.

If we suppose that the degree of association is the same for the two temperatures T_1 and T_2, then the general equation

$$S_1(xMv_1)^{\frac{2}{3}} - S_2(xMv_2)^{\frac{2}{3}} = 2{\cdot}12(T_2 - T_1) \quad \ldots\ldots\ldots(3)$$

is obtained.

Hence $x^{\frac{2}{3}}\{S_1(Mv_1)^{\frac{2}{3}} - S_2(Mv_2)^{\frac{2}{3}}\} = 2{\cdot}12(T_2 - T_1)$;

$$\therefore\ x^{\frac{2}{3}} = \frac{2{\cdot}12(T_2 - T_1)}{S_1(Mv_1)^{\frac{2}{3}} - S_2(Mv_2)^{\frac{2}{3}}},$$

$$x = \left[\frac{2{\cdot}12(T_2 - T_1)}{S_1(Mv_1)^{\frac{2}{3}} - S_2(Mv_2)^{\frac{2}{3}}}\right]^{\frac{3}{2}}.$$

EXERCISE 16.

Emulsifying Power: Use of Donnan Pipette.

The **Donnan pipette** (see Fig. 22) consists of a tap **T**, bulb **B** of (say) 5 c.c. capacity, capillary tube **C**, and wider tube drawn out into a point **P**, which is ground off flat.

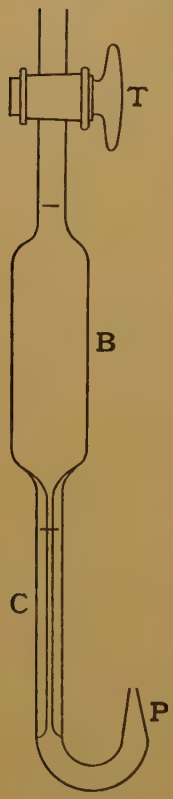

FIG. 22.

Fill the pipette with light-petroleum to a point above the top mark, and close **T**. Clamp the pipette vertically with the point **P** immersed to a certain depth in water. Open **T**, carefully adjusting it so that the drops issuing from **P** rise at a convenient rate. There should be sufficient room in the pipette above the top mark, otherwise before the adjustment is completed the surface of the oil may have fallen below the mark. Having obtained a suitable rate for the stream of drops, begin to count them when the surface of the oil inside the pipette reaches the top mark, and continue counting until the lower mark is reached. The number of drops, and therefore the size of each drop, is fixed by the difference in the specific gravity of the two liquids and by the surface tension which acts round the circumference of the point and tends to retain the drop.

Repeat the experiment, substituting for water aqueous solutions of sodium carbonate, sodium hydroxide and soap as far as time will permit.

A diminution of surface tension tends to increase the number of drops (and therefore diminish the size of each), and corresponds with an increase in the emulsifying power of the liquid. Marked froth-forming power is an indication of high emulsifying power in a solution, both being associated with a reduced surface tension in the case of the solution compared with the solvent.

This method has been applied by Dubrisay (*Comptes Rendus*, 1913, *156*, 894-898) to the determination of acidity of a liquid by running in standard alkali from a pipette, the point of which dips in the liquid, and counting the number of drops per volume of alkali. The number of drops shows a marked increase at the neutral point.

MEASUREMENTS OF THERMOCHEMISTRY (INTRODUCTION).

A CHEMICAL change is usually accompanied by the evolution or absorption of a measurable amount of heat. Quantity of heat is determined by measuring the effect produced on the temperature of a standard substance (water).

The unit employed in measuring heat is 1 **calorie** or 1 **cal.**, which is the heat required to raise 1 gram of water 1° above $t°$. This quantity varies with the temperature t; according to some authorities (Rowland 1878, Callendar and Barnes 1899 and 1902),

the 15° calorie $(t = 15°) = 4{\cdot}184 \times 10^7$ ergs,
20° „ $(t = 20°) = 4{\cdot}180 \times 10^7$ „
25° „ $(t = 25°) = 4{\cdot}177 \times 10^7$ „

The mean calorie $= \frac{1}{100}$ of the heat required to raise 1 gram of water from 0° to 100° C. $= 4{\cdot}184 \times 10^7$ ergs.

Other authorities give values differing from these.

In view of these figures the **laboratory calorie** ($t°$ = Room Temperature; in the case of Thomsen's experiments 18° to 20°) may be taken $= 4{\cdot}180 \times 10^7$ ergs or 4·180 joules without introducing too great an error.

Other units are: 1 **large calorie** = 1 Cal. = 1000 cals.,
1 **centuple calorie** = 1K = 100 cals.

The Specific Heat of a substance = quantity of heat absorbed by 1 gram of the substance when its temperature is raised 1° C. **The Heat Capacity** of any weight of a substance is the quantity of heat absorbed by that weight when its temperature is raised 1° C.

A cylindrical vessel (**calorimeter**) is used to hold the water (or solution), the temperature of which is raised or lowered as the result of heat evolved or absorbed by the materials undergoing the change being studied. The change under observation in some cases is made to take place within the water (*e.g.* heat of solution and heat of neutralisation), in other cases inside a vessel immersed in the water (*e.g.* calorimetric bomb method).

The heat effect can be calculated from the temperature change, and the specific heat and the weight of the water (or solution).

Account must, however, be taken of:

(*a*) the heat absorbed or evolved by the calorimeter, the stirrer and the part of the thermometer immersed in the water;

(*b*) the rate of heat exchange with surroundings;

(*c*) the error due to evaporation.

To correct for (*a*), determine **the water equivalent of the apparatus**.

Let w_2 = weight of calorimeter and s_2 its specific heat; let w_3 = weight of stirrer and s_3 its specific heat; let x c.c. = volume of that part of thermometer immersed in water and s_4 = the heat capacity per unit volume for glass or mercury. Then, the heat required to raise the whole apparatus 1° is

$$w_2s_2 + w_3s_3 + xs_4,$$

which is called the "**water equivalent**" of the apparatus

According to the material employed in constructing the apparatus, one or more of the following specific heats will be required.

Pt 0·032, Ag = 0·056, Brass 0·092, Cu 0·093, Ni 0·109, Glass 0·160.

The **heat capacity per c.c.** for glass or mercury = 0·47. If w_1 is the weight of water in the calorimeter, then the heat required to raise the water + the whole apparatus 1° is

$$w_1 + w_2s_2 + w_3s_3 + xs_4.$$

Determination of the Volume of the Immersed Part of the Thermometer.

Run some water into a burette and take a reading of the level of the water. Immerse the thermometer in the water to the same point as in the calorimeter. Observe the new level of the water. The difference between the two readings is the volume of the water displaced by the thermometer. In the case of a Beckmann thermometer, the volume must be determined in 2 parts, first the part containing the bulb, and then the part of the stem above the bulb. The second part has not a solid wall, and the external volume is, therefore, not the sum of the glass-volume and the mercury-volume, and so, about $\frac{1}{5}$ of the measured external volume should be taken as the sum of the glass-volume and the mercury-volume, and this figure added to the volume of the bulb part gives the required total.

Effect of Rate of Stirring.

Richards (*Journal of American Chemical Society*, 1910, 431), in experiments on heat of solution, found in using a plunger stirrer that, whilst vigorous stirring was necessary, 60 strokes per minute gave adequate mixing, and it was not advisable to employ a higher rate which increased too much the error due to heating caused by stirring.

When the rate of stirring is doubled, the heat generated is increased ten-fold.

To reduce the rate of heat exchange with the surroundings, the calorimeter **C** (see Fig. 23) is polished on its outer surface and is placed inside, but insulated from a nest of heat jackets **M**, of polished metal, and insulated from one another by air spaces and wooden insulators **I**. The outer jacket **W** is usually double-walled, and water is filled in between the walls some hours before the experiment, so that the surroundings of the calori-

meter may be in a state of heat equilibrium. Also, the outer surface is covered with felt. For very accurate measurements it is important, for some measurements it is essential to maintain the experiment room at a uniform temperature. It is impossible here, however, to go into details further in this direction.

Again, lids **L** of insulating material are placed on the heat jackets to prevent air currents, and thus reduce the rate of heat exchange with surroundings.

To reduce the error due to evaporation, the calorimeter is also covered with a lid of non-conducting material.

The calorimeter is made of material (*e.g.* silver or copper) of high heat conductivity, so as to obtain as quickly as possible uniform distribution of heat throughout the whole calorimeter.

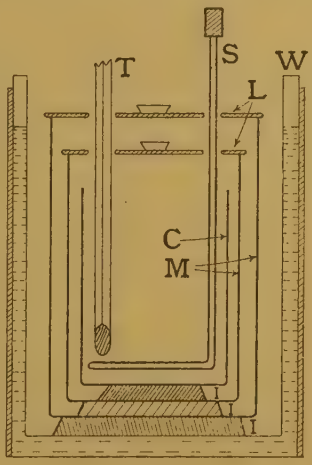

FIG. 23.

The dimensions of the calorimeter are chosen so as to reduce as far as possible both (*b*) rate of heat exchange with surroundings and (*c*) loss due to evaporation. For general calorimetric work, the height is made equal to $1{\cdot}25 \times$ diameter; however, a height greater than this is often found more convenient in Thermochemistry. For example, a copper cylinder 5 ins. high, 3 ins. diameter and about 560 c.c. total capacity, gilded inside, will serve for many purposes.

Of the total heat, the fraction absorbed by the calorimeter water should be great compared with that absorbed by the stirrer, thermometer, etc. About 400 c.c. to 500 c.c. of water are used. The total volume of the calorimeter should therefore be comfortably over this figure.

A thermometer graduated in $\frac{1}{100}^{\circ}$ is used for measuring the rise or fall of temperature, and it is better to measure a small temperature change with a good Beckmann rather than a large temperature change with a less reliable instrument. This lends additional support to the use of the fairly large quantity of water already referred to. Again, it is well to avoid a high rise of temperature, as the error due to radiation is greater, and more difficult to correct for, the greater the temperature difference.

The calorimeter and the outer water jacket are provided with stirrers.

The calorimeter in thermochemical work may be made of silver (gilded inside), platinum, copper (gilded inside), nickel, aluminium or nickel-plated brass.

The error due to heat exchange with the surroundings should be got rid of as far as possible by a suitable arrangement of the experimental details. This is best attained with an adiabatic calorimeter. With the ordinary experimental methods already described, an error due to radiation still remains, and the necessary correction is obtained by a calculation, graphical or arithmetical (see under Heat of Neutralisation).

If the temperature of the surroundings is kept the same as that of the water in the calorimeter, then radiation inwards or outwards is prevented. This is what is aimed at in the adiabatic apparatus devised by Richards (*Jour. Am. Chem. Soc.*, April, 1910, page 431), and modified by Benedict and Higgins (*Jour. Am. Chem. Soc.*, April, 1910, page 461).

The new form of adiabatic mantle described below has been found very convenient by the present writer, and may find a more extended usefulness. The general arrangement of the apparatus will be understood from Fig. 24.

The dimensions in Fig. 24 are given in inches. Fig. 24 is a vertical section of the outer and the inner can. The outer can (12 × 9) is connected by means of $\frac{1}{2}$ inch horizontal tubes with a vertical tube (8 × 2), shown at the left, in which rotates

a turbine stirrer. This stirrer may be driven by a small 2 to 4 volts motor, and produces very efficient mixing. On the right, fixed on, opposite a slit, is shown a tube for holding a Beckmann thermometer. To the inner surface of the outer can near the top are fixed 3 little metal blocks placed symmetrically. In the figure, for clearness, two blocks are shown directly opposite one another; this would involve the use of 4 blocks in all, but 3 at regular intervals suffice. To each block is

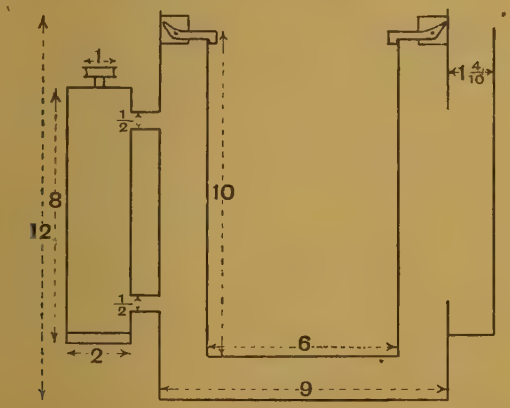

FIG. 24.

hinged a short lever; when removed in one direction one arm of the lever comes against the inner surface of the outer can, thus preventing the little lever from going beyond the horizontal position. The other arm is turned down at the point, and when in the horizontal position keeps the inner can (10 × 6) in place, when water is in the mantle. Thus a fairly stable arrangement is obtained, and the inner can may be removed easily when required. For greater stability, it would be well to have in addition small wooden blocks between the bottoms of the outer and inner cans.

A flexible copper tube $\frac{1}{4}$ inch internal diameter, and about 8 feet long, is soldered at the ends to short brass tubes $\frac{7}{16}$ inch

external diameter. The flexible tube itself does not make a water-tight joint with rubber tubing. Short brass tubes $\frac{1}{16}$ inch external diam. are soldered in through the wall, near the top of the larger outer can, and these are connected by means of rubber tubes with the brass ends of the flexible, which, passing from the inlet, coils round near the wall of the larger can in the form of a spiral till the bottom is reached, when it rises almost straight up to the outlet.

Water is put into the space between the two large cans. The space in which the calorimeter is placed is thus surrounded by a jacket of water on all sides except the top. The problem of screening the top with water will be referred to later.

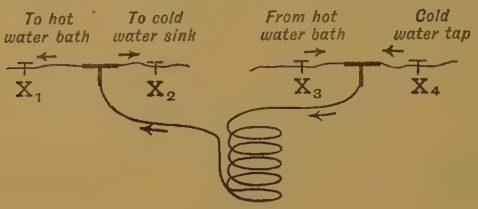

FIG. 25.

The temperature of the jacket-water depends upon the stream of water in the flexible, and this stream is controlled by a system of T-tubes and taps, the arrangement of which is shown in Fig. 25. $\mathbf{X}_1$, $\mathbf{X}_2$ and $\mathbf{X}_3$ are glass taps with bore of about 3 mm., and for $\mathbf{X}_4$ a fixed metal water tap may be used, provided it has no leather washer. To obtain a stream of cold water, the taps $\mathbf{X}_1$ and $\mathbf{X}_3$ are closed and $\mathbf{X}_4$ (the water tap) and $\mathbf{X}_2$ are opened, the stream being regulated with the taps according to the rate of cooling required. To obtain a stream of hot water, $\mathbf{X}_2$ and $\mathbf{X}_4$ are closed and $\mathbf{X}_3$ and $\mathbf{X}_1$ are opened as far as required. The stream of hot water is pumped with a Luther pump from a hot water bath, which may be conveniently heated by means of an asbestos woven wire net, placed between the bath and a layer of bricks. A net of wire of S.W.G. $33\frac{1}{2}$,

of about 220 ohms for use with 220 volts mains, will usually suit. Frequently, about 5 to 6 litres of water maintained at about 50° C. will serve as a hot-water bath. If it is necessary to heat the bath with a flame and also to avoid the use of gas in the measurement-room, then an inlet and an outlet tube can easily be led through the wall to the neighbouring room, where the bath can be erected.

All the metal parts of the apparatus except the flexibles should be made of brass nickel plated. It is advisable that the flexible should be of copper which has a high heat conductivity.

With the above apparatus, the temperature of the water-mantle can be made to rise or fall at any rate likely to be required, and thus radiation prevented inwards to, or outwards from the calorimeter.

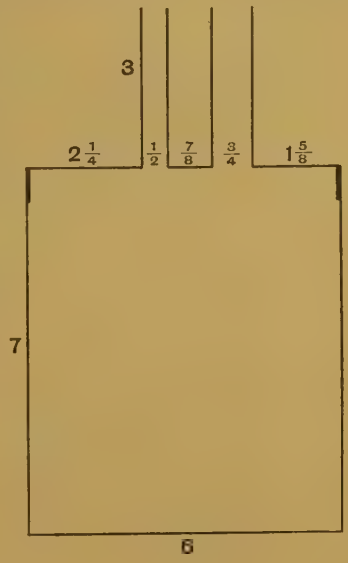

FIG. 26.

The present form of adiabatic mantle, provided, as it is, with only an ordinary cover on the top, is a great improvement on the ordinary non-adiabatic mantle. For many purposes, this, the simplest form of adiabatic mantle, will suffice. For very great accuracy, however, it is necessary that the top-side also should be provided with a water screen, the temperature of which is under control.

The top water screen is best obtained with the submerged form of inner can. With this form, not only is the inner space almost completely surrounded by a water mantle, but the mantle temperature is regulated with comparative ease by

means of a stream of water through only one flexible. The submerged can may be made 6 inches in diameter and 7 inches in height, with a water-tight lid provided with three tubes 3 inches high—two $\frac{3}{4}$ inch tubes and one $\frac{1}{2}$ inch tube. Two of the tubes are seen in Fig. 26. All three are shown in the horizontal section in Fig. 27. These tubes give access to the interior of the mantle without having to remove the lid. The $\frac{1}{2}$ inch tube is for the stem of the rotating stirrer dipping in the liquid in the calorimeter placed inside the mantle. One $\frac{3}{4}$ inch tube is for a Beckmann thermometer, the other is for receiving a narrow test-tube or the stem of a funnel or any similar piece of apparatus.

FIG. 27.

This set of tubes is very convenient for several kinds of Thermochemical experiments. The outer can is also provided with an ordinary cover, having three holes through which pass the three tubes of the submerged can. This sunk can is held in position, so that the lid is well under the surface of the water, use being made of the three little levers referred to above together with corks of a suitable size.

EXERCISE 17.

Construction of a Thermostat.

The supply of gas to a gas-heated thermostat must be regulated automatically.

Fig. 28 shows a vertical section of the regulator and a horizontal section of the large glass bulbs. The filling of the apparatus is very simple, and will be readily understood from the figure. The large bulbs with their vertical tube, also

part of the small **U**-tube, are filled with 10% $CaCl_2$, a little mercury being placed in the **U**-tube before connecting with the $CaCl_2$ bulbs. The connection at **F** is by means of rubber tubing. When the temperature rises above a certain value, the narrow end of the tube at **D** is closed by the rising mercury, so that the gas entering at **A** can reach the heater of the thermostat only by way of **B**. When the temperature falls

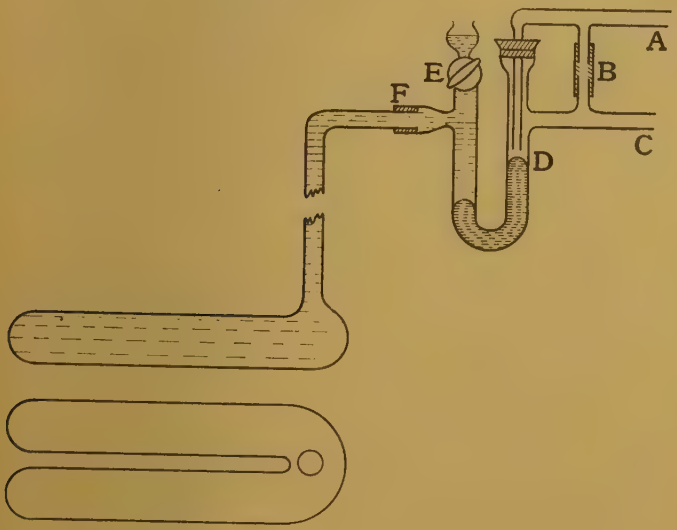

FIG. 28.

below the same value, the gas can pass by two channels, by **B** and **C** and by **D** and **C**, and thus the temperature is raised. The adjustment can be conveniently obtained by leaving the tap **E** open until the required temperature is almost reached and then adjusting the height of **D**.

The large glass bulbs rest on the bottom of the thermostat, and as much of the little **U**-tube as possible is immersed in the water. The necessary number of small acetylene gas burners consuming ordinary gas may be used to heat the bath.

The stirring may be effected by means of a turbine stirrer clamped to the side of the thermostat, and driven by a small electromotor.

EXERCISE 18.

Heat of Neutralisation.

The ordinary apparatus as shown in Fig. 23 and Fig. 29 may be used. In Fig. 23, **C** is the cylindrical calorimeter, which may be of copper gilded inside (total capacity about 560 c.c., diam. 3 ins., height 5 ins.). **M, M** are metal heat-jackets with lids **L, L** of heat insulating material. **W** is a water heat-jacket covered on the outside with felt. **B** is a Beckmann thermometer. Instead of **S**, the ordinary stirrer, use a rotating stirrer: a small inverted perforated thistle funnel rotated by a 2 to 4 volts electric motor will serve very well. **I, I, I** are made of wood and heat-insulate the jackets from one another.

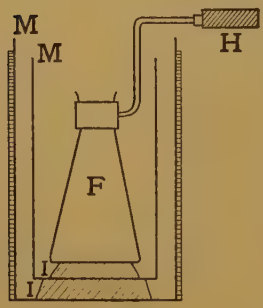

FIG. 29.

In Fig. 29, **F** is a conical flask with a wooden handle **H**, and **M, M** are metal heat-jackets.

Set two Beckmann thermometers so that the reading is near the bottom of the scale at Room temperature, and compare the readings of the two thermometers for the same temperature. Take one thermometer as the standard, and correct the readings on the other. From the stock n.HCl prepare 1000 c.c. $\frac{n}{4}$ HCl, and add 200 c.c. of $\frac{n}{4}$ HCl to the calorimeter and 100 c.c. of water. From the stock n.NaOH, prepare $\frac{n}{2}$ NaOH. Wet the inside of the conical flask with a little of the $\frac{n}{2}$ NaOH, and then add 100 c.c. $\frac{n}{2}$ NaOH, and place the conical flask inside a couple of heat-jackets, as in Fig. 29.

Place one Beckmann in the HCl solution in the copper calorimeter, so that the bulb reaches half-way down the liquid, and start the stirrer. Wet the lower part of the other Beckmann and place it in the $\frac{n}{2}$ NaOH in the conical flask.

Note the readings on the Beckmann's every minute for 7 minutes. Then pour the alkali into the acid quickly, but avoid splashing. Note the exact time of mixing, stir and note temperature every minute. Plot temperature against time, and a curve is obtained as in Fig. 30. By extrapolation, we see that the temperature of the alkali at the moment of mixing is t_1, and the temperature of the acid is t_2. After mixing, the temperature suddenly rises, and after 3 minutes steadily falls, a straight line indicating the change of temperature. Extrapolating from this line, we see that the mixture would have risen to t_3 had there been no radiation.

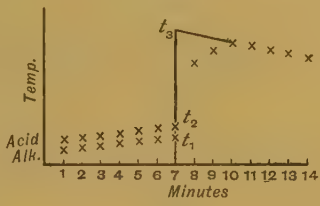

FIG. 30.

Thus 300 c.c. of NaCl solution have been raised from t_2 to t_3,
and 100 c.c. ,, ,, ,, ,, t_1 to t_3.

Let s = specific heat of the sodium chloride solution,
d = density of NaCl solution,
w = water equivalent of calorimeter, stirrer and thermometer.

$$\text{Heat evolved} = sd\,300(t_3 - t_2) + sd\,100(t_3 - t_1) + w(t_3 - t_2).$$

$\frac{n}{8}$ NaCl has a density at 18°-20° of less than 1·0118, and specific heat greater than 0·978.

By putting $sd = 1$, an error of less than 1 % is introduced.

If heat evolved = H, then heat of neutralisation = $5 \times 4 \times H$, this being the heat evolved when an equivalent of sodium hydroxide is neutralised by an equivalent of hydrochloric acid.

The above method, in which a smaller bulk (100 c.c.) of more concentrated alkali is added to a larger bulk (300 c.c.) of less concentrated acid, will be found of general application in the comparison of heats of neutralisation of various acids (some perhaps sparingly soluble) with the same strong alkali. Also the smaller conical flask used in this method will be found more convenient to handle than the usual larger flask, and there will be less danger of error due to splashing and due to heat losses during transferring of liquid from one vessel to the other.

If the adiabatic mantle already described is used here, then there will be no need for correcting for radiation error. The simplest form of adiabatic mantle should prove very satisfactory.

The error is $\pm 2\%$.

EXERCISE 19.

Heat of Solution of a Solid.

Use an apparatus similar to that for heat of neutralisation. Fit the calorimeter with a motor-driven stirrer and a thermometer, and through a hole in the lid put a thin-walled glass test-tube, resting on a small wire-gauze basket hanging from the lid. The basket is preferably made of platinum, but gilded-copper gauze will generally suit. In the test-tube put a glass rod. Weigh into the calorimeter 400 grams of water. Weigh the test-tube, and into it weigh enough finely powdered KNO_3 to give with 400 grams of water a solution of the strength 1 gram mol. of solute to 200 gram mols. of water. Place the test-tube containing the salt and glass rod in position in the calorimeter, start the stirrer, take the temperature every minute, and allow the test-tube time to acquire the temperature of the water. With the rod, break the test-tube, and allow the salt to be washed down into the basket, never stopping the stirrer and continuing to record the temperature. Plot the temperature against the time as before, and determine the change of temperature of the water. Vigorous stirring is necessary to accelerate the rate of solution. If the substance dissolves

very slowly, then, for accurate work, an adiabatic apparatus should be used.

Let t_1 = initial temperature and t_2 = final temperature of the water, and let the water equivalent of the calorimeter, stirrer, test-tube and thermometer be W.

Let
m = mol.wt. of KNO_3,
w = weight of KNO_3 dissolved,
s = sp. ht. of solution,
d = density of solution.

Then heat of solution of one gram molecule

$$= \frac{m}{w}(t_2 - t_1)(400ds + W),$$

$d = 1{\cdot}0173$ and $s = 0{\cdot}966$.

Repeat the experiment with KI, making a solution of same molecular concentration, also with anhydrous $CuSO_4$ and with $CuSO_4 . 5H_2O$, in the case of the last two substances making the concentration 1 gram mol. in 400 gram mols. of water. From the last two results, calculate the heat of hydration of copper sulphate.

A student would require two laboratory periods to carry out all these measurements, so that different students should work with different substances and compare results.

Error is $\pm 2\%$.

EXERCISE 20.

Basicity of an Acid (Thermometric Method).

Weigh 0·25 gram of succinic acid into a calorimeter. Add water and stir mechanically until the acid is completely dissolved. When the temperature is steady, run in $\frac{n}{4}$ NaOH from a burette, with constant stirring, taking simultaneous ,burette and Beckmann thermometer readings. Plot the temperature

readings against the burette readings, and note where there is a marked bend in the curve. This indicates the neutral point.

EXERCISE 21.

Heat of Precipitation.

Fit up a calorimeter with a protecting mantle, either in the ordinary or the simplest adiabatic form.

Suspend a thin-walled test-tube in the calorimeter as in the heat of solution experiment. Also provide a stirrer and Beckmann thermometer for the calorimeter liquid. Place 400 c.c. of water in the calorimeter, and dissolve in this a little over 0·6 gram of sodium chloride. Into the test-tube pour 10 c.c. of normal silver nitrate solution. Place the test-tube and rest of the apparatus in position and stir.

When the temperature is constant, break the test-tube with the glass rod and mix the silver nitrate solution thoroughly with the sodium chloride solution. Observe the change in temperature, and calculate the heat of precipitation.

The figure obtained is the heat of solution with the sign reversed. On passing from 18° to 34°, the solubility of silver chloride is doubled. Using the formula

$$\log C_2 - \log C_1 = \frac{Q}{2R} \frac{T_2 - T_1}{T_2 T_1},$$

calculate the value of Q from these data, and compare the calculated with the experimental result.

HEAT OF COMBUSTION.

THE heat of combustion of a substance is the heat evolved by the complete combustion of a gram molecule of the substance.

The reaction is usually made to take place in compressed oxygen inside a "**calorimetric bomb**."

The main source of error in this measurement is the loss of heat by radiation. This is best overcome by an adiabatic mantle, such as that described above. The whole apparatus must, however, be modified to suit this particular experiment.

The following details refer to the Benedict and Higgins apparatus, in which the heating is electrical and the cooling is by means of water.

The dimensions of the apparatus with a bomb of maximum height 23·2 cms. and maximum diameter 8·8 cms. should be as follows:

A Calorimetric Can, to contain water in which the bomb is to be immersed, is made of nickel-plated brass 24·5 cms. high and 13 cms. diam.

A Stirrer, to move in the water in the calorimetric can, to consist of 2 flat brass rings, encircling the bomb, perforated by a number of holes and held together by several small brass rods, 10 cms. long. The stirrer is to be raised and lowered by 2 rods made of hard rubber. There are brass eye-joints on each rod to allow the stirrer flexibility of motion and prevent binding.

The calorimetric can rests on 3 hard-rubber guides and knife-edges.

Intermediate Can, about 13 mm. from inner can, 31·0 cms. high and 15·3 cms. in diameter, and made of nickel-plated brass.

Outer Can, 35·5 cms. high and 19·0 cms. in diam., and made of nickel-plated brass.

In the space between the intermediate and the outer can is placed water, the temperature of which is regulated by heating electrically or by cooling with a current of water. (This may be modified, as indicated above, by heating or by cooling with a current of water passing through a copper flexible tube.)

Illustration of a Determination of Heat of Combustion.

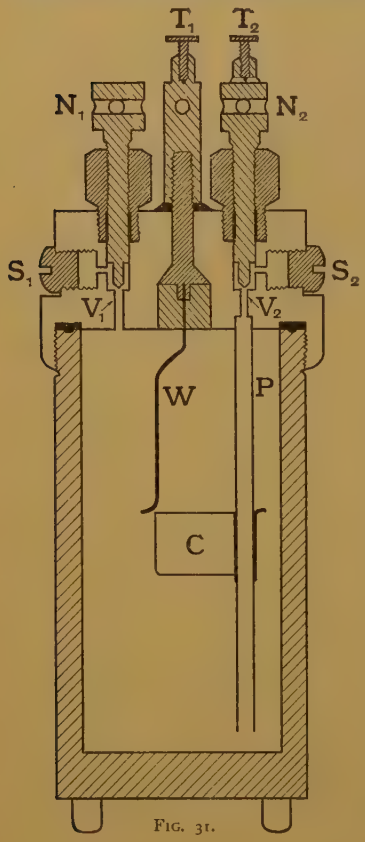

FIG. 31.

Make a capsule of cane sugar (see tabloid press, page 51). Let the weight = 1·2905. The substance must not be in the form of a powder, since part of the substance may be thrown out and escape combustion. Unscrew the nickel-plated strong cover of the bomb, remove and place on a stand in an upright position, taking care not to bend the wire **W** (see Fig. 31). Place the crucible **C** in position and place the capsule in the crucible. Weigh a piece of thin iron wire 0·1 mm. diam. and 6 to 7 cms. long, wind into a spiral and attach to wire **W** and platinum tube **P**, and press down the spiral to touch the sugar in the crucible.

Vaseline the screw of the cover, and also the lead

washer. See that surfaces of contact are free from grit. Screw the iron bomb-holder on the bench, and in its 3 holes place the 3 feet of the strong nickel-plated steel bomb. The bomb is enamelled inside, and to protect the enamel place a nickel cylindrical beaker loosely fitting inside the bomb. Place the washer and cover on the bomb, and with the double armed key, screw the cover down.

Close the valve $\mathbf{V}_1$ by turning $\mathbf{N}_1$ and the valve $\mathbf{V}_2$ by turning $\mathbf{N}_2$ (large force not necessary). Take out the screw $\mathbf{S}_2$ in the cover and connect with the oxygen cylinder and the manometer. Open the valve on the oxygen cylinder slowly (avoiding a sudden thrust of pressure on the manometer) till the manometer shows that gas is being emitted. Then open $\mathbf{V}_2$ a little, and let gas enter the bomb slowly till the manometer indicates 25 atmospheres.

Close $\mathbf{V}_2$ and the valve on the oxygen cylinder, and disconnect the oxygen cylinder, and replace the screw $\mathbf{S}_2$. Listen for any leak, and if necessary make the lid and the valves air tight.

Weigh into the calorimetric can, say, 2125·8 grams of water. Connect the terminals $\mathbf{T}_1$ and $\mathbf{T}_2$ with the poles of a battery of (say) 6 accumulators by means of wires and a key $\mathbf{X}$, the key $\mathbf{X}$ being in the meantime left open. By means of a strong string through the hole in the central pillar lower the bomb down into the calorimetric water. Hang a "set" Beckmann in the water and place the cover and the stirrer in position. Place a "set" Beckmann also in the adiabatic mantle water in the tube at the outside.

Make the calorimetric temperature 2° below room temperature, since a rise of 2° is reckoned on, and the final temperature should be near the room temperature. Start stirrer, applying to plunger stirrer about 60 strokes a minute. With electric heating and water cooling (Benedict and Higgins' method) make jacket about 0·1° lower than calorimeter, which can be maintained at a constant temperature within 0·001° for some

minutes. The jacket should be colder than the calorimeter to compensate for heat from outside through tubes, etc., in the cover. When the temperature has remained constant for some minutes, turn on the switch for heating, and pass the current so long that the water jacket will ultimately be raised to the temperature expected in the calorimeter. After the current has passed for 45 seconds (say), take a calorimetric reading and ignite the substance by closing the key **X**.

The jacket heating is started first because the heating coil acts slowly. After a minute the calorimeter and jacket temperature rise at the same rate. After ignition the 2 thermometers are watched, and if the temperature of the jacket does not follow the temperature of the calorimeter, the temperatures are kept the same by electric heating or stream of cold water. A careful regulation of the initial period of heating will render this equalisation of the temperature scarcely necessary. Three or four minutes after the ignition, the temperature of the water jacket reaches a maximum, which remains constant as long as desired.

(The above details refer to Benedict and Higgins' apparatus, these being given because the results shown below were obtained with this apparatus. However, the same method is applicable with slight modifications to the adiabatic apparatus previously described, in which heating and cooling were effected by a stream of water passing through a copper flexible tube.)

When the temperature of the calorimeter is constant, remove the bomb from the calorimeter, unscrew $\mathbf{S}_1$ and open slowly $\mathbf{V}_1$, allowing the gaseous products of combustion to escape. These may be analysed by passing them through a set of absorption tubes, as in an ordinary organic elementary analysis for determination of C and H.

Unscrew the cover, examine the crucible to see if all the substance has been burned, wash out the bomb with dilute alkali, then with water, and finally dry.

Weigh any unburned iron wire, and subtract the weight found, from the original weight. If corrected weight $= w$, then

$w \times 1600$ cals. is due to the combustion of w grams of iron, and must be subtracted from the experimental result. It may be that there is formation of nitric acid from some nitrogen present in the oxygen, and in very accurate work this must be corrected for thus: Wash out the bomb with water, boil to expel CO_2 and titrate wash water. In the formation of 1 gram molecule of aqueous nitric acid about $1{\cdot}43 \times 10^4$ cals. are evolved.

Calculation.

Weight of cane sugar,	1·2905
Weight of water in calorimeter,	2125·8
Water equivalent of bomb,	374·2
	2500·0

Time.	Temp. of cal. water.	Temp. of mantle water.	
3·30	18·430	18·36	
3·31	18·430	18·38	
3·32	18·430	18·38	(started heating coil).
3·33	18·430	18·66	(start of combustion).
3·34	19·200	19·60	
3·35	20·420	20·33	
3·36	20·478	20·45	
3·37	20·479	20·46	
3·38	20·479	20·49	

End temp., - -	20·479
Initial temp., - -	18·430
Rise, - - -	2·049
Thermometric correction,	+0·008
Total rise, - -	2·057

$$2{\cdot}057 \times 2500 = 5143 \text{ cals.}$$

Let 35 cals. = correction for Fe and HNO_3, then 5108 is obtained. $\frac{5108}{1{\cdot}2905} = 3958$ cals. per gram.

The water equivalent of the bomb is determined experimentally by carrying out a combustion of a substance, the heat of combustion of which is already known; for example:

Substance.	Heat of combustion per gram.
Benzoic acid	6322 cals.
Naphthalene	9640 „

Thermochemical Data.

Heat of combustion per gram.

Cane sugar 3950 cals.

Heats of neutralisation (Wörmann, 1905).

·25*n*NaOH and ·25*n*HCl at	6°	$1{\cdot}43 \times 10^4$ cals.
	18°	$1{\cdot}37 \times 10^4$ „
	32°	$1{\cdot}30 \times 10^4$ „
·25*n*NaOH and ·25*n*HNO_3 at	6°	$1{\cdot}44 \times 10^4$ „
	18°	$1{\cdot}37 \times 10^4$ „
	32°	$1{\cdot}29 \times 10^4$ „

Heats of solution at 18° (Thomsen).

1 gram mol. of solute in	Solute.	Heat of solution.
200 gram mols. of water	KNO_3	$-\ 8{\cdot}52 \times 10^3$ cals.
200 „ „	KI	$-\ 5{\cdot}11 \times 10^3$ „
400 „ „	$CuSO_4$	$+15{\cdot}80 \times 10^3$ „
400 „ „	$CuSO_4 \cdot 5H_2O$	$-\ 2{\cdot}75 \times 10^3$ „

Specific heats: see page 71.

Latent heats of vaporisation: see page 55.

„ „ **fusion**: see page 59.

VELOCITY OF REACTION.

Hydrolysis of Methyl Acetate in presence of HCl.

Prepare 500 c.c. of $\frac{n}{20}$ NaOH from 25 c.c. n NaOH.

Prepare 100 c.c. of $\frac{n}{2}$ HCl from 50 c.c. n HCl in CO_2-free water.

Clean two small Erlenmeyer flasks with steam and dry. Fit with corks (soaked in melted paraffin) and weight with lead. There are required also one or two Erlenmeyer flasks of about 100 c c. capacity for titrations; also 3 pipettes of 1 c.c., 2 c.c. and 20 c.c. capacity, and a small stoppered bottle containing pure methyl acetate.

Into one of the small Erlenmeyer flasks, pipette 20 c.c. of $\frac{n}{2}$ HCl, and place it in a thermostat at 25°. Also place the bottle containing the methyl acetate in the thermostat.

When the liquids have reached 25° (after, say, about 10 minutes), pipette 1 c.c. of the methyl acetate into the HCl flask. Shake, and at once withdraw 2 c.c. of the mixture, and in order to retard the reaction velocity as far as possible, deliver the 2 c.c. into about 30 c.c. of CO_2-free water, placed in one of the conical 100 c.c. flasks. Titrate the acid in the 100 c.c. conical flask as soon as possible with $\frac{n}{20}$ NaOH. The moment when the 2 c.c. are mixed with the water is taken as the starting point of the reaction.

After about 10 minutes again withdraw 2 c.c. of the HCl mixture, check the reaction by pouring into water, and titrate

as before. Record the exact time at which the 2 c.c. are mixed with the larger bulk of water. This is the time corresponding with the titration.

Go through the same procedure at points of time 20, 30, 40, 60, 120 minutes from the starting point of the reaction, and after the mixture has been left in the thermostat for 48 hours, carry out a final titration.

The equation $$k = \frac{1}{t} \log_e \frac{a}{a-x},$$

or $$k = \frac{2{\cdot}30}{t} \log_{10} \frac{a}{a-x},$$

should hold for this unimolecular reaction, where a is the initial concentration of ester and $a-x$ is the concentration after time t.

Let titration readings after intervals

$$t,\quad t_1,\quad t_2,\quad t_3$$

be $$T,\ T_1,\ T_2,\ T_3.$$

Let initial titration reading be T_0, and reading at final time t_∞ be T_∞;

then a is proportional to $T_\infty - T_0$,

and $a-x$ „ „ $T_\infty - T$;

$$\therefore\ k = \frac{2{\cdot}30}{t} \log_{10} \frac{T_\infty - T_0}{T_\infty - T},$$

also $$k = \frac{2{\cdot}30}{t_y - t_x} \log_{10} \frac{T_\infty - T_x}{T_\infty - T_y}.$$

Thus, to calculate k, it is not necessary to calculate from the titration readings the amount of ester hydrolysed, but the value of k can be obtained by the direct use of the titration readings.

A similar experiment with $\frac{n}{2}$ H_2SO_4 may be carried out alongside of the above, and a corresponding value of k found.

The ratio of the values of k gives the ratio of the strengths of HCl and H_2SO_4.

EXERCISE 22.

Solubility of Carbon Dioxide in Water.

Henry's Law:

When a gas is in contact with a given quantity of a liquid, the weight of gas dissolved at a given temperature is proportional to the pressure of the gas.

If the volume of the weight dissolved in 1 c.c. is expressed at the pressure and temperature of the experiment, then the result is the **Solubility.** Call this λ.

If the volume is calculated which would be dissolved in 1 c.c. of the liquid if the pressure of the gas were 760 mm., and if the volume thus calculated were reduced to N.T.P., *i.e.* to 0° C. and 760 mm. pressure, then the final result would be the **Absorption Coefficient** for the temperature of the experiment. Call this A.

If the temperature of the liquid is $T°$ abs. and if the pressure of the gas is p mm., and if V c.c. of liquid absorb v c.c. of gas measured at p mm. and $T°$ abs., then $\lambda = \frac{v}{V}$.

If the pressure of the gas were 760 mm., then v would become $v \times \frac{760}{p}$. Reduce this to 0° C. and 760 mm., and we obtain

$$v \times \frac{760}{p} \times \frac{p}{760} \times \frac{273}{T}$$

or

$$v \times \frac{273}{T}.$$

Thus

$$A = \frac{v}{V} \times \frac{273}{T}$$

and

$$A = \lambda \times \frac{273}{T}.$$

Place the apparatus in a Mercury Tray. In the apparatus (see Fig. 32) there are a 3-way tap **Z**, a 3-way tap **Y**, a 2-way tap **X**, gas burette **B** and solubility vessel **C**.

By **Y** connect **E**, **C** and **F**; then open **X**.

Dip **X** in air-free water, allowing the water to fill **C**; close **X** and **Y**. Remove **C** from the water, and by opening **X** and **Y** allow the water to flow into a measuring vessel, and in this way find the volume of **C** (call this volume v_1 c.c.).

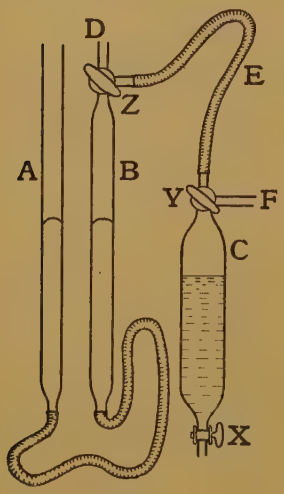

FIG. 32.

Fill **C** with water as before and close **X** and **Y**.

Keep **Y** closed, and by **Z** connect **B**, **D** and **E**, and by raising **A** fill **B** to **Z** with mercury. Connect **D** with a CO_2 gas holder. By **Z** connect **D** and **E** but not **B**, and by **Y** connect **E** and **F** but not **C**, and allow gas from the holder to flow from **D** to **E**, then to **F**.

Shut **Y**, and by **Z** connect **B**, **D** and **E** and by lowering **A**, fill **B** with CO_2.

Keep **Y** closed, and by **Z** connect **B** and **E** but not **D**. Allow to stand for about 20 minutes. Adjust **A** and read level of mercury in **B** (call this reading r_1). Let barometric reading be h and let temperature of burette be T_1° absolute.

Place the measuring vessel under **X**; open **X**, connect **C** and **E**, but not **F**, by means of **Y**. Raise **A** and allow water to run into the measuring vessel (let v_2 c.c. be run out). Then the volume of the remaining water $= (v_1 - v_2)$ c.c.

Shut **Y**. Shake the absorption vessel **C**. Open **Y** and read the burette. Repeat until a constant reading is obtained. Let this reading $= r_2$ c.c.

In every case, before the equilibrium point is finally determined, the solubility vessel should be kept in a bath at a constant temperature. Let this temperature $= T^\circ$ abs., and let the vapour pressure of water at that temperature $= p$. Then,

whereas the volumes read on the burette are at pressure h and temperature T_1, the pressure in the solubility vessel is $(h-p)$ and the temperature is T. Thus, if we reduce the burette readings to the solubility vessel conditions, we obtain instead of $r_1 - r_2$,

$$(r_1 - r_2)\frac{h}{h-p}\frac{T}{T_1}.$$

Therefore, volume of gas absorbed $= (r_1 - r_2)\frac{h}{h-p}\frac{T}{T_1} - v_2$ and the volume of water $= (v_1 - v_2)$ c.c., and 1 c.c. of water absorbs $\dfrac{(r_1 - r_2)\frac{h}{h-p}\frac{T}{T_1} - v_2}{v_1 - v_2}$.

This assumes that the gas in the burette is dry and that the gas passes only in one direction—from burette to solubility vessel—and that the temperature of the burette and the barometric pressure are constant during the experiment.

This result gives the **solubility** of the gas in water at temperature T and pressure $(h-p)$. Call this λ. Calculate the volume of gas absorbed when the pressure of the gas is 760 mm. Also, reduce the volume so found to the value obtained when measured at 760 mm. and 0° C. This result is the **absorption coefficient**. Call this A. Then $A = \lambda \times \frac{273}{T}$.

In the case of the more soluble gases, such as CO_2, be careful not to allow too much gas to enter the solubility vessel, as the absorption may cause the mercury to enter the solubility vessel. It is convenient to have **B** large and **C** small for the more soluble gases, such as carbon dioxide and nitrous oxide, and to have **B** small and **C** large for the less soluble gases, such as oxygen, hydrogen and nitrogen.

For very accurate work, both **B** and **C** should be provided with jackets containing water maintained at a constant temperature.

Preparation of Gas-free Water.

Place distilled water in a round-bottomed distillation flask having a side tube, connected with a reflux condenser by rubber tubing fitted with a screw clip (see Fig. 33). The flask and the condenser are evacuated by means of a water pump, and the water is kept boiling until on shaking the flask

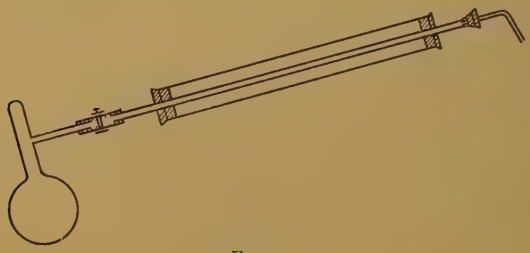

Fig. 33.

a metallic sound indicates that the water is gas-free. Close the screw clip tight. Remove the condenser, and in its place put the absorption vessel fitting the tube at **X** into the rubber tubing. Keep the screw clip closed, open **X** and exhaust the solubility vessel. Then close **Y** and open the screw-clip, allowing the gas-free water to enter the solubility vessel, heating the water if necessary.

EXERCISE 23.

Solubility of Solids: Influence of other Electrolytes on the Solubility of Silver Acetate.

If two electrolytes have an ion in common, the presence of one *diminishes* the solubility of the other. If two electrolytes have no ion in common, the presence of one *increases* the solubility of the other.

Thoroughly clean 5 stoppered bottles of about 150 c.c. capacity. In each place about 1·25 grams of silver acetate.

To the first add 100 c.c. of water.

„ second add 100 c.c. of $\frac{n}{20}$ $AgNO_3$ solution.

„ third add 100 c.c. of $\frac{n}{20}$ sodium acetate solution.

„ fourth add 100 c.c. of $\frac{n}{20}$ acetic acid solution.

„ fifth add 100 c.c. of $\frac{n}{20}$ potassium nitrate solution.

Allow each bottle to sit in a thermostat at about 50°, shaking them occasionally. Remove each, cool a little and close with a rubber stopper. Rotate for 2 hours in a thermostat at 20°. Place on a shelf in the thermostat, allowing the solid to settle.

With a piece of rubber tubing, attach to a 25 c.c. pipette a filtering cap consisting of a short piece of glass tubing blown at the end into a perforated bulb in which is put a plug of cotton wool, or asbestos or glass wool, to filter the solid from the solution (see Fig. 34).

FIG. 34.

Pipette out 25 c.c. of solution from the first bottle and determine the amount of silver by titration with $\frac{n}{20}$ NH_4CNS, using ammonium iron alum as indicator.

Proceed similarly with the other solutions, and compare the results. Silver nitrate and sodium acetate each have an ion in common with silver acetate, and therefore *diminish* the solubility. Acetic acid should have the same effect, but on account of its low degree of dissociation the influence is so slight as to be within the experimental error. Again, potassium nitrate should *increase* the solubility, but the effect is not appreciable.

Owing to **adsorption**, the first portion of solution passing through the filtering cap has its concentration changed. The error arising from this, however, is very slight.

Instead of an ordinary pipette, a graduated density pipette may be used so that the density of the solutions can be determined at the same time.

If only one laboratory period is available for this experiment, different students should work with different substances and compare results.

EXERCISE 24.

Approaching an Equilibrium Point from Opposite Directions.

With the same apparatus as in the preceding experiment:

(1) Place 1·25 grams of silver acetate in 100 c.c. of water and rotate in the thermostat at 20° without previous heating. After 2 hours determine the solubility, as in preceding experiment.

(2) Place 1·25 grams of silver acetate in 100 c.c. of water. Leave for some time in a thermostat at, say, 50°, cool slightly and rotate in a thermostat at 20°. After 2 hours determine the solubility.

In (1) the equilibrium concentration is approached from a lower concentration. In (2) the equilibrium concentration is approached from a higher concentration. For true equilibrium, the two results should be the same.

SPECTROSCOPY (INTRODUCTION).

THE refractive index varies according to the colour of the visible rays, the red being least deviated or refracted and the violet most refracted.

Behind a vertical slit in a metal screen place a source of white light, that is, light which contains all the colours. Place a convex lens of 10 inches focus at about 12 inches in front of the slit. On the side of the lens remote from the slit, move a vertical screen until a sharp image of the slit is obtained upon it. Now place a prism, with its edge vertical, between the lens and the screen. The image of the slit is no longer seen on the screen. Move the screen until the deviated light again falls on the screen. The image is now coloured, or rather a continuous series of coloured images of the slit is obtained. Make the image sharp by adjusting the position of the screen. The coloured band is called a **spectrum.**

Now, slowly rotate the prism, keeping the edge vertical; the spectrum will be seen first to move to the right (say), then stop, then move to the left. The position of the prism corresponding to the turning-point is called the position of **minimum deviation,** and the band obtained in this position is more brightly and clearly coloured, and less bent than in any other position. The spectrum obtained in this way is not **pure.** In other words, it consists of several overlapping bands.

This is because the light falls on the prism at different angles, and the deviation depends on the angle at which the light strikes the prism. To obtain a **pure spectrum,** all the rays incident on the prism should be parallel. Therefore, a convex

lens is placed between the prism and the slit, with the slit in the focus of the lens. The light then falls in parallel rays on the prism, the red rays emerging from the prism in parallel rays in one direction, the yellow rays in parallel rays in another direction, the blue rays in another, and so on. Thus the colours do not overlap, and a pure spectrum is obtained. Between the prism and the screen another convex lens is placed, and the screen is put in its focus. This lens receives parallel rays, which are therefore focussed on the screen. It is convenient to place this lens near the prism, though for focussing it is not necessary to do so. This arrangement (see Fig. 35,

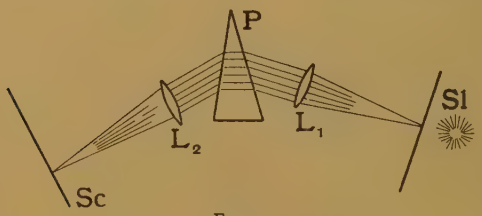

FIG. 35.

which shows the refraction for only one colour of rays) of *slit* **Sl**, *lens* $\mathbf{L_1}$, *prism* **P**, *lens* $\mathbf{L_2}$ and *screen* **Sc** constitutes a **spectrometer**, an instrument for analysing the light emitted by a luminescent body.

The light will often yield on analysis not a continuous band, but a set of coloured images of the slit, separated from one another by dark regions; in other words, there is obtained what is called a **line spectrum**. The number and colour (or wave-length) of the lines are characteristic of the substance emitting the light. The identification of even one of the lines emitted by an unknown substance implies identification of the substance.

A photographic plate in the focus may be substituted for the screen, or a cross-wire in the focus and an eye-piece in front, the second mentioned lens $\mathbf{L_2}$ and the cross-wires and eye-piece forming a **telescope.**

A tube with the first-mentioned lens L_1 mounted in one end and the slit in a tube sliding in the other end is called the **Collimator.**

The tube containing the cross-wire and eye-piece is usually moved, for focussing, by means of a rack and pinion, and in this tube the eye-piece slides so as to be focussed on the cross-wire. In the instrument, to be now described, instead of the above rack and pinion, a milled ring on the body of the telescope is used, which, when rotated, moves the object glass.

When a collimator is used, it is not necessary to place the prism of a spectrometer in the minimum deviation position to obtain a pure spectrum. However, in measuring and comparing wave-lengths of spectrum lines, the prism must be always in the same position, and, as the minimum deviation position is one which is most easily reproduced, it is the one always used.

EXERCISE 25.

Measurement of Wave-lengths of Lines of Line Spectra.

In the **Hilger Wave-length Spectrometer** (Constant Deviation Type), a compound prism is used which may be imagined to be built up of 3 right-angled prisms (see Fig. 36).

ABD, ABC, DCE are 90°.
ADB and **DEC** are 60°.
DAB and **CDE** are 30°.
BAC and **BCA** are 45°.

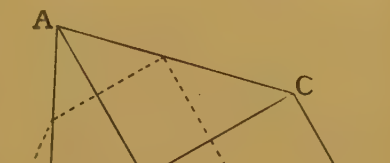

Fig. 36.

When a ray of light enters **ADB** at the proper angle for *minimum deviation*, it travels parallel to **DB** and at right angles to **AB**, is totally reflected at **AC**, travels at right angles to **BC** and is refracted out at **DE**. It travels through both **ADB** and

DCE at minimum deviation; therefore the ray emergent from the compound prism is at right angles to the ray incident on it. Thus, if we find that a ray in passing through this compound prism has been deviated through a right angle, then we know that the ray must have passed through at minimum deviation. Therefore, in this instrument, the collimator and the telescope are fixed permanently at right angles to one another, and the prism is placed on a turn-table, by rotating which different lines of the spectrum can be thrown on the intersection of the cross-wires. Whatever light falls on the intersection of the cross-wires at any moment has been deviated through 90°, and therefore must have travelled through the compound prism at minimum deviation. It is not, of course, necessary to make the compound prism in three parts. In fact, it is made in a single piece of glass.

The prism turn-table is rotated by means of a fine steel micrometer screw, the point of which is of hardened steel and presses against a steel plug in a projecting arm on the prism table. This steel plug is flint-hard and optically polished. To the screw is attached a helical drum, on which the wave-length of the line at the intersection of the cross-wires is read.

When the screw is turned clockwise, the point presses against the steel plug, pushing the lever round, but when the screw is turned counter-clockwise, a spring presses the plug up against the point, and if for any reason the spring does not act, and therefore the plug does not follow the point, *care must be taken that the plug does not fly up against the point*, as in this way the point may be damaged and apparent periodic errors produced in the screw.

Note also never to touch the polished surfaces of the prism with the fingers.

In setting the wave-length drum be careful to *approach the reading by turning the drum right-handedly*. This instruction must be attended to in order to get the most accurate results,

on account of the impossibility of making absolutely perfect fittings, and especially the impossibility of making the perfect screw, upon which the present movement depends for its accuracy.

In the ordinary form of spectroscope the collimator is fixed, the prism is put in the position of minimum deviation and the telescope is moved, bringing various lines into the field of vision. Corresponding to each line a reading is taken, either on a divided circle or on an illuminated arbitrary scale. The readings of a large number of known lines are plotted against their wave-lengths, a curve being obtained called a "map." The reading of an unknown line is then fitted to its place in this curve, and thus the wave-length is graphically determined. This must, however, be regarded merely as a method for the qualitative identification of a line, unless a very expensive instrument is used and a long time devoted to the experiment.

The Hilger Constant Deviation Spectrometer already described gives the wave-length directly, and is to be recommended on account of the ease and speed with which a determination can be carried out. In using the dense prism supplied by Hilger, the errors for various wave-lengths are as follows:

Wave-length in Å.U.,	4000	5000	6000	7000	8000
Average error in Å.U.,	1	1	1·6	3	5

Before carrying out a measurement, shift the eye-piece until the cross-wires are in focus. Place the telescope and collimator in their fittings, and clamp the prism gently in the position marked on the turn-table. Illuminate the slit with the light from a sodium flame, the slit being made very narrow. By means of the screw on the helical drum rotate the turn-table until the reading opposite the arrow on the drum is 5896 Å.U. as nearly as possible. (The readings may be obtained with a special telescope.) Imagine the cross-wires to be at the same distance as the object, and by turning the milled ring (or the rack and pinion) obtain a sharp image of the sodium D lines.

If the adjustment is correct, when the eye is moved in front of the eye-piece, the cross-wires and image show no relative displacement. Look through the eye-piece, and if necessary unclamp the prism, and gently move the prism to bring D_1 line (whose wave-length is 5896 Å.U) on the intersection of the cross-wires. Now move the drum-screw until the D_2 line is seen on the intersection of the cross-wires. The reading should now be 5890. The D_1 and D_2 lines will not be seen as separate lines unless the focussing is correct and the slit sufficiently narrow.

The lines obtained with a prism spectroscope are always more or less bent, because the collimator lens can render the light parallel to the axis only if the light comes from the centre of the slit.

Measure the wave-lengths of the chief spectrum lines of the following, looking out for the ones indicated and focussing in each case with the milled ring to obtain a clearly defined line:

	Wave-length in *Ångström Units.*	*Rydberg's Symbols.*
Sodium.	D_1 yellow 5896·1	$[P_2 \cdot 1]$
	D_2 yellow 5890·2	$[P_1 \cdot 1]$
Lithium.	red 6708·2	
Potassium.	red 7701·9	$[P_2 \cdot 1]$
	red 7668·5	$[P_1 \cdot 1]$
	violet 4047·4	$[P_2 \cdot 2]$
	violet 4044·3	$[P_1 \cdot 2]$

$[P_1 \cdot 1]$ means that the line is number 1 of the 1st *Principal series.*

$[P_2 \cdot 1]$ means that the line is number 1 of the 2nd *Principal series.*

D_1 and D_2 thus form the first pair of the *Principal series of pairs of lines* found in the sodium spectrum. Similarly, the above two red lines of potassium form the 1st pair and the two violet lines the 2nd pair of the Principal series of pairs in the potassium spectrum.

To obtain the illumination, dip a clean platinum wire in hydrochloric acid, then in the salt, and hold in the edge of the flame of an ordinary Bunsen, or better, of a Méker burner. Similarly, a piece of charcoal may be used instead of platinum. Or the flame may be fed by an asbestos wick dipping in a solution of the salt, or by a spray rising from a solution submitted to electrolysis. A convenient form of spray-fed burner is shown in Fig. 37.

Platinum wire or charcoal may be used with sodium chloride and lithium chloride; platinum wire should be used with potassium nitrate. The examination of the spectrum of sodium

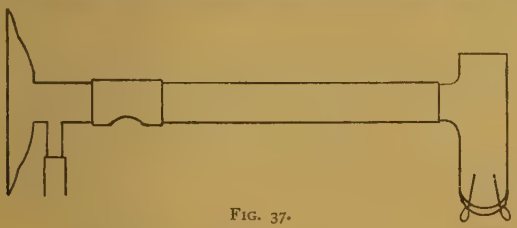

FIG. 37.

and lithium may be carried out easily by one person. For potassium it will be necessary to have a second student feeding the flame while the first is taking a reading; heat a thin platinum wire, dip in powdered potassium nitrate and hold in the edge of a Bunsen flame. The potassium nitrate melts, forming a bead and then bursting into a flame which yields lines sufficiently bright for this work. The red and violet lines of potassium are interesting and important, being at the extreme ends of the visible spectrum, and an effort should be made to catch sight of them while the flame lasts. It may be necessary, however, to repeat the feeding of the flame several times before the lines are seen.

For further practice, the spectra of the following should be examined: hydrogen, thallium, strontium, calcium, the carbon arc alone, the carbon arc fed with salts (*e.g.* those of lithium and magnesium) and the mercury arc.

Hydrogen: Pass a discharge from an induction coil through a **Plücker hydrogen tube**, which is placed in the vertical position with its capillary part opposite the slit. Look for 6563 (red), 4860 (green) and 4340 (blue).

Thallium: Heat thallium chloride with a platinum wire in the edge of a Bunsen. Look for 5351 (green). *Do not allow the fumes of the thallium chloride into the air of the room.*

Strontium and calcium: It is impossible without some experience to identify the lines: there are so many.. Use a Bunsen and look for 4607 (blue) from Sr and 4227 (blue) from Ca.

Carbon arc: Focus on the slit the light from a carbon arc.

Lithium in arc: Look for 6102 (orange) and 4603 (blue).

Magnesium in arc: Look for 5183, 5172 and 5167 (green).

Mercury arc: Focus on the slit the light from a quartz mercury tube; *great care must be taken to protect the eyes from the ultra-violet rays.*

REFRACTIVE INDEX (INTRODUCTION).

When a ray of monochromatic light passes from one medium to another of different density, the direction in which the light travels in the first medium is, for all directions but one, different from that in the second. If the path in the first medium makes an angle ϕ_1 with the normal to the common surface, and the path in the second medium makes an angle ϕ_2 with the same normal, then $n_1 \sin \phi_1 = n_2 \sin \phi_2$ (see Fig. 38), where n_1 is a constant depending on the nature of the first medium and n_2 is a constant depending on the nature of the second medium.

Fig. 38.

If $\phi_1 = 0$, then $\phi_2 = 0$, that is, there is no change in direction.

n_1 is called the **refractive index** of the first medium, and depends on the colour of the light. We are really concerned with the ratio $\frac{\sin \phi_1}{\sin \phi_2}$, and in practice it is usual to take air as a standard of reference and put its refractive index equal to 1.

Thus, if the first medium is air,

$$\frac{\sin \phi_1}{\sin \phi_2} = n_2.$$

Rapid measurements of the refractive index are obtained with the **Pulfrich Refractometer,** in which is used a right-angled glass prism (refractive index $= N$), one side of the right angle forming the horizontal top. The central part of the top of the

prism is kept plane and the rest is ground into a spherical surface (see Fig. 39). There is also a short thick-walled glass tube open at both ends, and having one end ground into a spherical surface of the same curvature as that on the prism. A glass block is provided, on which is ground a spherical surface of the same curvature. Thus the curved surface on the end of the tube fits the surface on the top of the prism and the curved surface on the block. The tube must be fixed to the prism with a cement; fish glue, seccotine, or soluble glass may be used. Care must be taken to select a cement which is not acted on by the liquid to be placed in the tube. A very little cement is put on the curved surface at the end of the tube, which is then placed on the curved surface of the block and turned with gentle pressure, so that a uniform very thin layer of cement is obtained on the end of the tube, which is then fixed with gentle pressure on the top of the prism.

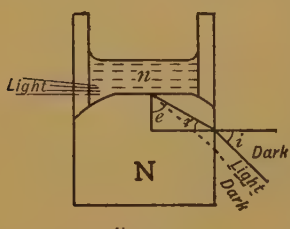

FIG. 39.

The liquid to be examined is placed in the tube. The ray of light enters horizontally and emerges in a direction making an angle i with the horizontal. The angle i is measured. If the refractive index of the liquid is n and that of the prism glass is N, we obtain $n \sin 90° = N \sin e$ (see Fig. 39).

$$N \sin (90 - e) = \sin i$$

or

$$N \sin r = \sin i;$$

$$\therefore \quad n = N \sin e = N \cos r = N\sqrt{1 - \sin^2 r} = N\sqrt{1 - \frac{\sin^2 i}{N^2}};$$

$$\therefore \quad n = \sqrt{N^2 - \sin^2 i}.$$

It is not necessary to carry out this calculation, as the makers of this instrument publish tables giving the value of n corresponding to any value of i.

EXERCISE 26.

Determination of the Molecular Refractive Power of Acetone.

(1) **Determine the density of acetone with a pyknometer.**

(2) **Determine the refractive index of acetone (for the D line).**

(1) Clean the **pyknometer** with potassium dichromate and sulphuric acid mixture, then with alcohol, then with redistilled ether. Then thoroughly dry by sucking in dry dust-free air, obtained by passing the air through a tube containing calcium chloride, then through a plug of cotton wool. Do *not* dry the pyknometer by heating. Weigh the tube, hanging it in the balance by means of a wire. Let weight $= w_1$. Attach a small rubber tube to a (Fig. 40), and dip b in distilled water and suck in water, filling the tube up to the mark in b. If too much has been sucked in, place a piece of porous paper (filter paper) against the opening at a, and allow the paper to absorb water until the mark in b is reached. Immerse the pyknometer in a thermostat at 25°. After a time, if necessary, again adjust the amount of water to reach the mark in b. Weigh the pyknometer + the water. Let weight $= w_2$. Empty the pyknometer, wash out repeatedly with acetone, and fill with acetone, as in the case of water, and weigh. Let weight $= w_3$; then

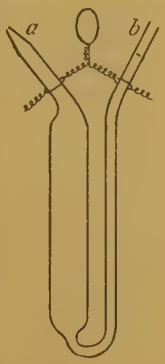

FIG. 40.

$$\frac{w_3 - w_1}{w_2 - w_1} = \text{density of acetone.}$$

Allowable error is unit in fourth decimal.

(2) In the form of **Pulfrich refractometer** described here (see Fig. 41), a telescope is placed with its axis at right angles to the ray emergent from the face of the prism. The ray is

admitted to the telescope through a slit in the side, and then reflected along the axis of the telescope. This slit may be covered completely with a shutter, as it should be when the instrument is not in use, or the right-hand half only may be covered (or the left half only), as should be the case when a divided cell is being used, or the whole slit may be left exposed

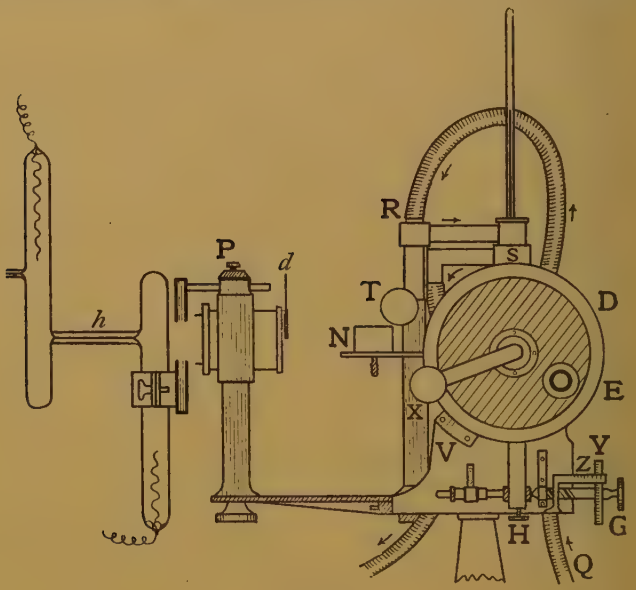

FIG. 41.

to the light. In Fig. 41 the eye-piece **E** of the telescope is seen in front of the disc **D**, to which the telescope is attached, the slit-end of the telescope being behind. The prism and the cell also are hidden by the disc **D** and are vertically below the thermometer, the top of which appears above the disc. This thermometer is fixed in the heater which dips in the cell, and which is lowered into position by turning the screw **T**. The arrows show the direction of flow of the heating water, which

first circulates through the prism's metal jacket (not seen in Fig. 41) and afterwards, as seen in Fig. 41, through the dipping heater **S**.

The prism is fixed on a cylindrical brass pillar in which is a triangular hole, and has a metal jacket on all sides except that facing the telescope, and at right angles to the disc **D**. Place the prism on the triangular pillar at the back of the instrument and tighten the screw (not seen in Fig. 41) in the cylindrical pillar, to fix the prism firmly in position. Slacken **H** and turn the telescope (the eye-piece of which is **E**), and the graduated circle **D** attached to it, round until the zero on the circle is opposite the zero on the vernier **V**, reading the scales with the lens **X**. Fix the circle in position by tightening **H**. Do not use more than a gentle pressure. By means of, say, a small electric lamp, illuminate the small right-angled prism p (in Fig. 42) seen let into the telescope near the eye-piece. A strong light should be used. This light is sent by the prism p along the telescope, it passes out at the slit, is reflected at the face of the prism and sent back along the telescope.

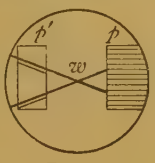

FIG. 42.

On looking through the prism there is seen (see Fig. 42), in addition to the cross-wires w, on the right the prism p, and on the left a bright rectangular patch which is the image of p. This image is usually seen to be crossed with two lines parallel to the cross-wires. These two lines are the images of the cross-wires. Turn the micrometer screw **G** until one image coincides with the corresponding cross-wire, then the other image ought to be coinciding with the other cross-wire. If this is the case, then the telescope is set at the correct zero. Observe the reading on the vernier, and introduce this as a correction throughout the experiment. If the two pairs of lines do not coincide simultaneously, it may be because the prism is not resting properly in its bed. Slacken the screw **K** in the prism's pillar, turn the prism in its bed, and observe the effect on the

field. Tighten **K** again and repeat adjustment. If it is still found impossible to obtain simultaneous coincidence, take the reading when one pair coincides and the reading when the other pair coincides. The mean of the two readings gives the zero.

On the micrometer screw **G** is a drum head **Y** graduated into 200 parts. When the drum is turned, it moves across a straight scale **Z**, each large division of which equals 60′ and each small division equals 20′. In a complete turn, the drum moves across one small division of the straight scale, and the telescope moves through 20′.

Thus 200 divisions on the drum are equivalent to 20′; therefore one division on the drum is equivalent to 0·1′. In taking micrometer readings, always notice to turn the screw in the same direction. The mechanism here is similar to that in the Hilger Constant Deviation Wavelength Spectrometer, and the remarks made in regard to it apply here also.

With a pipette place a little acetone in the cell, *taking care not to let the point of the pipette touch the flat surface of the prism.*

Place the wooden cap on the cell. Pass a stream of water at 25° (from a thermostat) in at **Q** round the metal jacket of the prism, from which it passes by a rubber tube to **R**, where it enters the dipping heater **S**, which is swung round and then lowered into the cell by turning the screw **T** as far as it will go, there being then still a layer of liquid between the heater and the prism. The water is led away by a rubber tube on the other side.

Place a sodium flame about 2 feet behind the prism **N**. Turn the prism **N** so that the light is thrown on the notch in the wooden cover of the cell. Slacken the screw **H**, and move the telescope and the divided circle round until a yellow band of light is seen in the field, and adjust until the upper edge of the band passes through as nearly as possible the inter-

section of the cross-wires. The upper edge corresponds with light entering the cell in a direction parallel to the plane top of the prism; the rest of the band is obtained from light entering the cell in other directions.

Having adjusted approximately by rotating the telescope, tighten the screw **H** and adjust exactly with the micrometer screw **G**. Focus the reading lens and take a reading, using a small light (a pocket electric lamp is very convenient) to render the scale visible, this being necessary if the experiment is carried out as it should be in a dark room.

The scale on the circle gives degrees and half-degrees. One division on the vernier is one minute. For example, $45\frac{1}{2}$ divisions on the circle and 23 on the vernier are equivalent to $45^\circ\ 30' + 23'$ or $45^\circ\ 53'$.

This angle is merely given as an example. It is not the angle for acetone.

In the maker's tables for the prism in use (I. *b*) we find under the heading *i*, the angle measured; under n_D, the refractive index of the liquid, calculated from

$$n = \sqrt{N^2 - \sin^2 i}.$$

Under Δ_n we find the amount to be subtracted from the last decimal place of n when the angle rises $1'$. The other columns give the corrections necessary when the light from C, F and G′ lines is used instead of D.

If it is desired to work with the C, F and G′ lines of hydrogen, then **N** is turned to the side, and the light from the hydrogen Geissler tube *h* is focussed, by means of the condenser **P**, on the notch in the wooden cover of the cell. Move down the diaphragm *d*, the edge of which is provided with a series of teeth which render indistinct the lower edge of the C, F and G′ bands. The coloured bands are narrowed also by the bottom of the dipping heater, and by the notch in the wooden cover of the cell.

The correction for temperature is obtained from the following table, supplied by Zeiss with their Pulfrich refractometer:

Correction in Units of the Fifth Decimal Place of n.

n	C	D	F
1·60	0·25	0·29	0·40
1·50	0·26	0·30	0·42
1·40	0·28	0·33	0·45
1·30	0·30	0·35	0·49

If t is the temperature, D the light and $n = 1{\cdot}34296$, then add to the number in the fifth decimal place of n the number obtained by multiplying $(t - 20)$ by 0·35.

Having found the density d and the refractive index n for acetone, calculate the **molecular refractive power** from the formula

$$\frac{n^2 - 1}{n^2 + 2} \times \frac{M}{d},$$

where M is the molecular weight.

Also calculate the **molecular refractive power** of acetone from the following **atomic refractive powers** for the D line:

Carbon singly bound	2·501
Hydrogen	1·051
Oxygen (in hydroxyl group)	1·521
Oxygen (in ethers)	1·683
Oxygen (in carbonyl group)	2·287

Find which value for oxygen gives a molecular refractive power nearest the experimental value.

The **Abbe Refractometer** depends on the same principles of grazing incidence and critical angle. It contains two right-angled glass prisms of high refractive power having acute angles each equal to 45°. A drop of liquid is placed on one hypotenuse, and the other hypotenuse is laid against the first, so that the two prisms form a rectangular block. A parallel beam of light entering at one side of the block is refracted into one prism and strikes the surface of the liquid at a certain angle of incidence, and is then refracted in the liquid, the angle of refraction being greater than the angle of incidence.

When the angle of refraction is 90°, the angle of incidence is the critical angle. For angles greater than this angle there is no refraction in the liquid, and the beam does not enter the second prism ; for angles less than the critical angle the light passes through the whole block, and comes out parallel to the original direction entering a telescope.

If the block is turned so that the incidence on the liquid is at the critical angle for a beam of light parallel to the axis of the telescope, then the field appears half light, half dark. To obtain this position, the prisms are moved until the critical dividing line between the light and the dark part of the field is brought to coincide with the cross-wires. The reading on the scale of the instrument then gives the refractive index of the liquid. The third decimal place is read, and the fourth can be estimated to two units.

When the block is set in this way, light parallel to the axis will pass through the two prisms and strike the telescope object lens in a direction parallel to the axis and be focussed on a point in the axis. Light in a direction at an angle to the axis may strike the liquid at an angle less than the critical angle, and thus pass through the block and emerge parallel to the original direction and be focussed by the objective lens on a point which, however, is not now on the axis. All such light goes to form the light half of the field. On the other hand, some of the non-parallel light may strike the liquid at an angle greater than the critical angle, and thus never reaches the telescope. All such light corresponds with the dark half of the field.

The light used should be monochromatic ; otherwise the critical line varies with the colour, and a coloured fringe is obtained. Compensating prisms are introduced into the telescope, which are rotated by a screw outside the telescope, and thus the dispersion can be obtained of the liquid for a light which is not monochromatic.

The Abbe Refractometer specially modified for a short range of values of refractive index is employed as a **butter refractometer**. Daylight is used, and the critical line is achromatised by the prisms themselves, when the substance examined has the same dispersive power as the standard.

Molecular refractive power, as the above shows, is partly **additive**, partly **constitutive**.

OPTICAL ACTIVITY (INTRODUCTION).

If ordinary monochromatic light, the vibrations of which are in all directions in the wave front, is sent through a **Nicol prism**, properly set, all the vibrations of the emergent light are perpendicular to one plane. Ordinary light has thus been **plane-polarised**. If a second Nicol prism, properly set, is placed between this plane-polarised light and the eye, and is rotated round an axis parallel to the line of vision, then there is a periodic change in the brightness of the field of vision, there being positions of maximum brightness followed after rotation through 90° by positions of minimum brightness or darkness. There are thus 2 positions of maximum brightness 180° from one another, and 2 of minimum brightness or darkness 180° from one another. The Nicol prisms are said to be **crossed** when the field appears dark. Before any of the plane-polarised light can pass through the second prism or **analyser**, either the plane of polarisation must be rotated or the analyser must be rotated. If the analyser is kept fixed in the crossed position and a tube of aqueous solution of cane sugar is placed between the polariser and the analyser, then the field no longer appears dark. This is due to the cane sugar, which must have rotated the plane of polarisation. If the analyser is now rotated through a certain angle, it passes into a position in which the field is again dark. This angle is the angle through which the cane sugar has rotated the plane of polarisation. The solution of cane sugar is said to be **optically active**.

There are two positions of darkness 180° from one another. If on turning the analyser through an angle less than 90° to the right (clockwise) darkness is obtained, then the active substance is said to be **dextro-rotary**; if the analyser has to be turned through an angle greater than 90° to the right to obtain darkness, then the dark field is also obtained by turning to the left through an angle less than 90°, and the active substance is said to be **laevo-rotary**.

The **polarimeter** is an instrument for measuring the angle through which an active substance rotates the plane of polarisation. Fig. 43 shows the general arrangement of the apparatus.

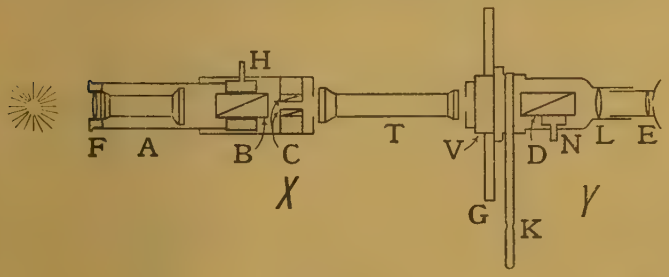

FIG. 43.

Monochromatic light (say, yellow light from a sodium flame) comes through a circular hole in a metal plate placed at focal length (say, 4 to 6 inches) from a lens **F**, which sends a nearly parallel pencil of rays through the tube **A** (containing a light-filter: a solution of potassium dichromate is used for sodium light), then through the polarising Nicol **B**. In the Landolt improved form of **Lippich polarimeter**, which is shown in Fig. 43, the two side parts of the polarised pencil emerging from **B** pass through the two small Nicols **C**. The whole pencil passes out from *X* by a small circular hole. It may then pass directly through a small circular hole into the tube containing the analysing Nicol **D**. The light is examined by means of a telescope, of which the object glass is **L** and the eye-piece **E**.

A clearly defined field can be obtained by adjusting the position of the eye-piece **E**, which is movable inside *Y*. To *Y* there is fixed a graduated disc **G**, with its centre in the axis of the tube and its plane at right angles to the axis. Turning the handle **K** which rotates the disc **G** past the stationary vernier **V**, in front of which is a reading lens, also rotates **D**, **L** and **E**. The difference between two readings on this circle gives the angle through which the analysing Nicol **D** has been rotated.

The substance to be examined is placed between the two tubes *X* and *Y*. If the substance is a liquid, it is placed in a thick-walled glass tube **T**, with ground ends on which fit glass plates, which are screwed against the ends of the tube with metal caps.

The two auxiliary Nicols **C** are used to obtain more accurate readings and to reduce the strain on the eyes. The middle part of the field is illuminated by light which in the polarising tube has passed only through the large Nicol **B**, and the two side parts by light which has passed both through the large Nicol **B** and through an auxiliary small Nicol. The field usually appears broken up into three parts, *either* two less bright side parts and a brighter middle part, *or* two brighter side parts and a less bright middle part. A reading is taken at the point where the three parts of the field are equally illuminated. On one side of this position the two side parts are in shadow, on the other side the central part is in shadow. The eye-piece is focussed to render sharp the lines of division between the parts of the field. In looking at one of the two lines of division, the portion of the eye on which the image of the bright part falls becomes fatigued, and if the two halves be suddenly made really equally bright, the half originally brighter would appear darker. Therefore, an inaccurate reading would be obtained. But if the eye is shifted from the one line of division to the other, the portion of the eye formerly fatigued is the portion on which the less bright light now falls. Thus the polarimeter having two auxiliary Nicols is an improvement of the ordinary Lippich form, where only one auxiliary

Nicol was used, and therefore only one line of division observed in the field of view.

There is, then, in the instrument described above, one position of the analyser for which no light passes through the central part of the field, and another position for which no light passes through the side parts. The angle between these two positions, the **half-shadow angle**, may be modified by shifting the handle **H** (see Fig. 43), and thus changing the relative setting of the large Nicol and the two small Nicols. The smaller the half-shadow angle, the greater the sensitiveness of the instrument. Usually an angle of about 5° is found convenient. **H** should never be shifted during an experiment, and only in exceptional cases will any other than the ordinary setting be required. The smaller the angle, the more difficult is it to discern the point of uniform illumination, and the more brilliant must be the light. If the liquid is turbid or coloured, it may be necessary to make the half-shadow angle larger than usual.

The position of the zero on the scale of the disc **G** depends on the setting of the analyser **D** in **V**, and this setting may be altered by moving the handle **N**. Two screws are provided for carrying out the adjustment. In this way, different parts of the scale may be used in examining the same liquid, and thus errors due to defects in graduation are diminished.

For the **Lippich** form of polarimeter, light of any single colour may be chosen, but the **Laurent** form, in which a quartz plate is used to obtain the half shadow, can be used only with light of one wave-length unless the quartz plate is changed.

The size of the angle of rotation depends on :

(1) The **nature of the substance** on which also depends the direction of the angle.

(2) The **length of the column of substance** through which the light passes.

(3) The **temperature**.

(4) The **wave-length of the light** used.

The shorter the wave-length, the greater the angle of rotation.

For examples of the influence of temperature see below. The influence of temperature is in many cases so small that if the room temperature does not change much, a bare observation tube may be used without any water jacket. Note, however, that the influence of temperature may be very important in experiments where velocity of reaction is being studied by this method. Here temperature influences not only the rotatory power but also the velocity of reaction, and when the experiment lasts for 2 or 3 days there may be considerable variations of room temperature. The temperature may be maintained constant by surrounding the observation tube with a water jacket in which circulates water at a constant temperature.

The **specific rotation** or **specific rotatory power** for sodium light at $25^\circ = [\alpha]_D^{25^\circ} = \frac{\alpha}{ld}$, where α = observed angle, l = length of column of liquid in decimeters and d = density of liquid. Molecular rotation $= [m]_D^{25^\circ} = m \times \frac{\alpha}{ld}$, where m = molecular weight.

For a solution of an optically active substance, when the solvent is not active,

$$[\alpha]_D^{25} = \frac{\alpha}{lw},$$

where w = weight of substance in 1 c.c. of solution and

$$[m]_D^{25^\circ} = m \times \frac{\alpha}{lw}$$

Usually $\frac{1}{100}$ of the above values of $[m]$ is taken and called the **molecular rotation.**

EXERCISE 27.

Determination of the Specific Rotation of Cane Sugar.

Dissolve 10 grams of cane sugar in water and make up the solution to 100 c.c.

Place some sodium chloride on a platinum gauze spiral, and rest the gauze on a support so that a Bunsen flame plays

on the sodium chloride. The flame should be behind a metal screen placed about 4 to 6 inches from the instrument, the light passing through a small circular hole in the screen.

Unscrew the metal caps from the *observation tube* and remove the small circular plates. Clean the glass plates and the tube. Place a glass plate on one end, and fix in position with the screw-cap, *avoiding using much force, as this might strain the glass* (causing elliptic polarisation). Fill the tube to overflowing with distilled water. Slide on the second glass plate, and fix in position with the screw-cap. The tube should be quite full; there should be no bubble of air. Place the observation tube in the groove between the polariser and the analyser. Rotate the *analyser* till the field is seen divided up into 3 parts, and adjust the eye-piece so that the lines of division between the different parts of the field are seen distinctly. Find the position when all three parts are equally illuminated. Adjust the lens on the right and take a reading. The experiment should be carried out in a dark room; therefore a small light will be required to render the scale visible: a pocket electric lamp is very convenient. On the circle each small division = 0°·25, and the vernier reads parts less than 0°·25. For example, 36° and 3 small divisions on the circle and 13 on the vernier is equivalent to 36°·75 + 0°·13 or 36°·88. Adjust the lens on the left and take a reading. The difference between the left and right readings should be 180°. The object of taking the two readings is to correct for eccentricity of the graduated circle.

Either of these readings may be taken as the zero of the instrument.

Empty the observation tube and wash out with a little of the sugar solution already prepared, and fill the tube with this solution. Place the tube in position and take right-hand and left-hand readings as before, adjusting the eye-piece again if necessary. Note the difference between the right-hand zero reading and the sugar right-hand reading. Also note the difference of the left-hand readings. The two differences should be

the same ; if not, take the mean. Note the length of the tube in decimetres and calculate the **specific rotatory power**. Note also whether the substance is dextro-rotatory or laevo-rotatory.

EXERCISE 28.

Velocity of Inversion of Cane Sugar.

The reaction is represented thus :

$$\underset{\text{cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6},$$

dextro-rotatory cane sugar changing to laevo-rotatory **invert sugar**, which is a mixture of glucose (dextrose) and fructose (laevulose). Fructose is more laevo-rotatory than glucose is dextro-rotatory ; therefore the chemical change is accompanied by a change of the sign of the rotation. The change is practically irreversible, and is very slow in pure water, but is accelerated in the presence of acids, to a degree which is nearly proportional to the concentration of the hydrogen ion. The progress of the change may be followed by measuring the angle of rotation from time to time.

The amount of cane sugar present at any time is proportional to the difference between the angle of rotation at that time and the angle of rotation at the end of the reaction.

If A_0 = the initial angle, A_∞ = the final angle, and A_n = angle after time t_n ; then

$$\frac{a}{a-x} = \frac{A_0 - A_\infty}{A_n - A_\infty},$$

and this being a unimolecular reaction, the concentration of water being comparatively constant,

$$k = \frac{2{\cdot}3^0}{t_n} \log_{10} \frac{A_0 - A_\infty}{A_n - A_\infty},$$

also

$$k = \frac{2{\cdot}3^0}{t_y - t_x} \log_{10} \frac{A_x - A_\infty}{A_y - A_\infty}.$$

The latter formula is the most satisfactory to apply.

Make 3 solutions: (1) Dissolve 20 grams of cane sugar in water, add a crystal of camphor as a preservative, and dilute to 100 c.c. (2) Prepare 25 c.c. of n. HCl solution. (3) Prepare 25 c.c. of n. H_2SO_4 solution. Throughout the experiment these 3 solutions are kept at a constant temperature (say 25°).

Take an observation tube provided with a water-jacket through which is pumped water at a constant temperature. Mix equal volumes of (1) and (2), and fill the observation tube with this mixture, but *the little filler-cup should be left empty.* Measure the angle of rotation, noting the time of reading. Take subsequent readings 5, 10, 20, 40, 60, 120 minutes after the first reading, and a final reading 48 hours later. Whatever the intervals are, the above formula gives the same value for k.

Let this value be k_1.

During the long interval of 48 hours, the observation tube may be kept immersed in the thermostat at 25°.

Repeat the above experiment, now mixing equal volumes of (1) and (3).

Let the value of k now be k_2.

When equal volumes of (1) and (2) are mixed, the normal hydrochloric acid becomes semi-normal, and similarly for sulphuric acid.

Comparison of k_1 and k_2 gives the relative strengths of the two acids.

k_1 in the above experiment is 0·00472.

The **inversion of cane sugar** in the presence of acids is not so simple a change as would appear from the above, nor as is generally supposed. Armstrong along with others (see Worley, *Trans. Chem. Soc.* 1911, *99*, 349) have pointed out complications arising from various causes. For example, acids have been found which not only alter the rate of inversion, but also change the specific rotatory power of the cane sugar and the invert sugar. This and other factors lead to unsatisfactory values for the final angle, when the assumption is made that the change is simply as usually represented.

The following formulae have been given for the specific rotation of cane sugar and for that of invert sugar:

For cane sugar:

$$[\alpha]_t^D = 66{\cdot}5 - 0{\cdot}0184(t - 20°).$$

(Schönrock, *Zeit. Instrumentenkunde* (1900), xx. 97.)

For invert sugar:

$$[\alpha]_t^D = -19{\cdot}66 - 0{\cdot}0361c' + 0{\cdot}304(t - 20°).$$

(Gubbe, *Ber. Chem. Ges.* (1885), *18*, 2214.)

c' = weight of invert sugar in 100 c.c. of solution and t = temperature. It will be observed that a term containing c' is introduced into the second formula and no concentration term into the first, concentration having more influence in the second case. Notice that t, temperature, also has a greater effect in the second case.

If c grams of cane sugar are dissolved in 100 c.c. of solution and become on inversion c' grams of invert sugar, then

$$c' = \frac{360}{342}c.$$

If α' = final angle and l = length of observation tube, then

$$\alpha' = -\{19{\cdot}66 + 0{\cdot}0361c' - 0{\cdot}304(t - 20)\}\frac{c'l}{100};$$

and if α = initial angle, then

$$\alpha = \{66{\cdot}5 - 0{\cdot}0184(t - 20)\}\frac{cl}{100}.$$

If the time available for the present experiment is limited, students may calculate the final angle from the above formula.

EXERCISE 29.

Determination of the Amount of Pure Cane Sugar in a Specimen of Impure Sugar.

(1) Prepare a solution containing about 15 grams of impure sugar (w grams) in 100 c.c. of solution, and determine the angle of rotation α.

(2) Take same weight, w, and at first do not add all the water, but only 10 c.c. of strong HCl, and heat at 70° for about 10 minutes, then cool and make up the solution to 100 c.c. at room temperature. Determine the angle of rotation α'.

Then, if β is the angle due to impurity, we obtain from the above formulae:

$$\alpha = \{66{\cdot}5 - 0{\cdot}0184(t-20)\}\frac{cl}{100} + \beta,$$

$$\alpha' = -\{19{\cdot}66 + 0{\cdot}0361c' - 0{\cdot}304(t-20)\}\frac{c'l}{100} + \beta,$$

where c' = weight of invert sugar from c grams of cane sugar; there being c grams of cane sugar in w grams of impure cane sugar,

$$\alpha - \alpha' = \frac{cl}{100}[\{66{\cdot}5 - 0{\cdot}0184(t-20)\} + \{19{\cdot}66 + 0{\cdot}0380c - 0{\cdot}304(t-20)\}1{\cdot}0526].$$

Hence c can be calculated. When the impurity is small, w may be substituted for c in $0{\cdot}0380c$. It is generally most convenient to neglect this term and, in this way, calculate c approximately, and then substitute this approximate value in the final calculation.

Organic substances having an **asymmetric carbon atom** are optically active, *natural optical activity* being a decidedly **constitutive property**.

FARADAY'S LAWS (INTRODUCTION).

When electricity passes round an unbroken circuit, the rate at which it passes through a cross section of the conducting material at any point in the circuit may be expressed as being a certain number of coulombs per second. For example, through a cross section of a wire we might have 4 coulombs passing per second. In other words, we say that the current is 4 ampères.

Coulombs per second = ampères

or *quantity* per second = *current.*

If 4 ampères last for 10 seconds, the *total* amount which has passed through *any* cross section is 40 coulombs. If 8 ampères last for 5 seconds, the *total* amount which has passed through *any* cross section is 40 coulombs. Thus, if there is any effect which depends on the quantity of electricity passed, then 4 ampères lasting for 10 seconds and 8 ampères lasting for 5 seconds produce the same effect. **Current** is the same at all parts of the circuit. **Current density** at any point in the circuit is equal to the **current** divided by the area of the cross section at that point.

According to Arrhenius' theory, though the ions due to the action of water on the electrolyte may be present in the solution in a state of irregular motion, they are uniformly distributed throughout the liquid. There is no drift of the ions as a whole in one direction more than in another.

When two charged masses of metal at different potentials (charged metallic plates, for example) are immersed in the solution, current passes, and the ions have, in addition to the

irregular movement already referred to, a drift as a whole towards the metallic plates (electrodes), the positively charged cations moving or migrating towards the **cathode** (the electrode at which the positive current leaves the solution), and the negatively charged anions moving or migrating towards the **anode** (the electrode at which the positive current enters the solution). *The electricity is conveyed by the ions.*

There may be more than one kind of anions, and, though they all share in conveying the electricity, it may be that they do not all lose their charge when they reach the anode. Similarly for cations. An ion can lose its charge at the electrode only in certain circumstances, to be explained in the study of E.M F.

The connection between the amount of any substance liberated and the *quantity* of electricity used is given in

Faraday's laws:

If an electrolytic cell forms part of an unbroken electric circuit, and if at one of the electrodes there is only one substance liberated in a given time, then the amount liberated at that electrode is proportional to the **total quantity of electricity** *passed through any cross section of the circuit, for example, through any cross section of the wire conducting the electricity to the electrolytic cell, and* **is independent of the rate at which the electricity flows.** *If two or more electrolytic cells are in series in the circuit, the same law holds with regard to the amount of substance liberated at any one of the electrodes in any of the cells. If two substances are simultaneously produced, the first being the only material formed at one electrode, and the second being the only material formed at another electrode in the circuit, then the amounts of these substances produced are in the ratio of their chemical equivalents.*

Every gram equivalent of cations in a solution is charged with $9{\cdot}650 \times 10^4$ coulombs of positive electricity or 1 faraday of positive electricity, and every gram equivalent of anions is charged with 1 faraday of negative electricity.

The symbols representing ions contain dots and dashes to indicate positive and negative charges respectively, the number of dots (or dashes) in the symbol showing the number of faradays per gram-ion or the number of equivalents per ion. The following are examples:

$$H^{\cdot}, Na^{\cdot}, Cu^{\cdot\cdot}, Fe^{\cdot\cdot\cdot}, Cl', NO_3', SO_4''.$$

Thus, when sodium chloride is dissolved in water, we have an equilibrium established represented by

$$Na\,Cl \rightleftarrows Na^{\cdot} + Cl'.$$

When 1 gram equivalent of cations is discharged at the cathode, $9{\cdot}650 \times 10^4$ coulombs of positive electricity (**or 1 faraday**) pass into the cathode, and at the same time $9{\cdot}650 \times 10^4$ coulombs pass through any cross section of the circuit, and let 1 gram equivalent of anions be at the same time discharged at the anode. The current at the surface of the cathode is completely cationic and at the surface of the anode completely anionic, but at any cross section of the liquid part of the $9{\cdot}650 \times 10^4$ coulombs is positive electricity passing in the positive direction, down stream, and part negative electricity passing in the negative direction, up stream; in other words, within the solution the current is partly cationic, partly anionic.

For example, we might have 48250 positive coulombs passing down stream and 48250 negative coulombs passing up stream, in which case the positive and negative ions would share the current equally. Again, we might have 77200 positive coulombs passing down stream and 19300 negative coulombs passing up stream, in which case the cations convey four times as much electricity as the anions.

The rate of drift of the cations is as a rule different from the rate of drift of the anions.

If 1 gram equivalent of a metal is deposited on the cathode, and if the amount of metal in the solution round the cathode has fallen only by $\frac{1}{3}$ gram equivalent, then $\frac{2}{3}$ gram equivalent

of cation must have migrated into the neighbourhood of the cathode. Thus the cations convey $\frac{2}{3}$ of the electricity and the anions $\frac{1}{3}$.

The fractions are called **Hittorf's Transport Numbers**. They may be written n_c and n_A, where, of course, $n_A = 1 - n_c$, and $\frac{n_c}{n_A} = \frac{U_c}{U_A}$, the ratio of the migration velocity of the cation to the migration velocity of the anion, or the ratio of the ionic conductivities $l_c : l_A$.

Thus, to obtain the Transport Numbers, it is necessary to know how many gram equivalents of any element have been liberated at an electrode either in the transport-number vessel or in some other electrolytic vessel in the circuit, and also to ascertain the accompanying change in composition of the solution round one of the electrodes of the transport-number vessel.

Note the influence of the following on Transport Numbers:

Current, Concentration, Temperature, Solvent.

Hittorf found that transport numbers were independent of the *Current.*

As the solution is diluted, a point is reached where further dilution produces no appreciable change on transport numbers.

Temperature influences transport numbers according to Kohlrausch. He found that, with monatomic univalent ions, the numbers approach 0·5 as temperature rises.

Solvent influences transport numbers, as the following shows:

With water as solvent, KCl, KBr, KI, all give $n_a = 0{\cdot}51$.
With phenol as solvent, KCl, KBr, KI, all give $n_a = 0{\cdot}19$.

EXERCISE 30.

Faraday's Law: Equivalence of Acids and Bases.

The apparatus is as in Fig. 44. **X** and **Z** are small beakers about 130 c.c. total capacity, 8 cm. high and 4·5 cm. diam. **Y** is an inverted **Y** tube, the two legs being about 9 mm. internal diameter and 9 cm. long. The **Y** tube is connected

above by means of rubber tubing, with a short tube containing a stop-cock. *V* is a **voltameter** or **coulometer**, containing a saturated solution of copper sulphate, in which dip a piece of platinum foil **P** (the anode) and a large piece of copper foil **C**, wound into a spiral (the cathode). When current passes through *V*, copper is deposited on **C** and oxygen is evolved

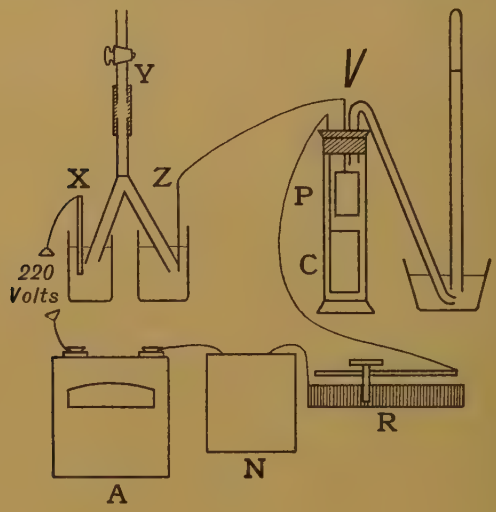

FIG. 44.

at **P**. This gas is collected and measured in a eudiometer tube reading to 100 c.c.

R is a variable resistance, and **N** is an asbestos woven-wire net of about 225 ohms resistance. **A** is an ammeter reading to 1·5 ampères.

Connect the terminals of *V* with cells, making **P** the anode and **C** the cathode, and pass current until the solution is saturated with oxygen. Half fill **X** and **Z** with a saturated solution of K_2SO_4. Fill the connecting tubes in **Y** by sucking at the top tube and closing the stop-cock. In **X** place a lead wire and in **Z** a nickel wire. Lead if used as cathode would

take up some alkali metal forming an alloy. Place the leading tube of *V* in position for collecting the oxygen. Connect the apparatus as in the figure, and regulate the current to obtain 0·3 amp. Allow the current to pass for about 20 minutes. Break the current, allow the syphon to run out. Lift the syphon from the liquid and rinse with a little distilled water, allowing the washings to run into the proper beakers. Titrate the whole of the anode liquid with $\frac{n}{10}$ NaOH (using phenolphthalein), and the whole of the cathode liquid with $\frac{n}{10}$ H_2SO_4. The number of equivalents of acid found in the anode liquid should equal the number of equivalents of alkali in the cathode liquid, and also equal the number of equivalents of oxygen evolved in *V*. $\frac{22{\cdot}41 \times 10^3}{4}$ c.c. is one equivalent of oxygen. Measure the volume of oxygen collected in the eudiometer tube, reducing the value to 0° and 760 mms. The number of c.c. obtained divided by $\frac{22{\cdot}41 \times 10^3}{4}$ gives the number of equivalents.

EXERCISE 31.

Determination of Transport Numbers.

The apparatus is as in Fig. 45, and is similar to that used in the last experiment. **Y** and the beakers **X** and **Z** are as before. **A** now has a range to 100 milliamps. The electrodes in **X** and **Z** are platinum plates of the usual form. The voltameter *V* consists of a vessel **G**, closed at one end with a rubber cork, through which pass a thermometer and two nickel wires, to which are firmly fixed two nickel plates which serve as electrodes. The vessel is connected at the other end to a burette by means of a rubber tube. The burette **B** reads to 50 c.c.

R is a variable resistance for regulating the current and **S** is a switch. About half-fill **X** and **Z** with $\frac{n}{100}$ H_2SO_4. Fill the

connecting tubes and close the tap above **Y**. Fill the voltameter with $2n$ NaOH and fix the rubber cork firmly in position. Pass current, using cells, until the liquid is saturated with hydrogen and oxygen. Allow the hydrogen and oxygen above the liquid to escape, adjusting the rubber stopper so that the liquid completely fills **G**. See that the level in **B** is not too

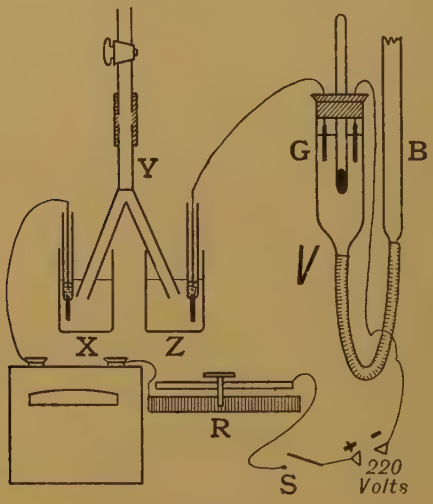

FIG. 45a

high, so that there may be room for the rise in the subsequent stage of the experiment. If necessary, pour out some of the liquid. Let the reading on the burette be r_1. Connect the apparatus as in the figure, and start the current. When the resistance **R** is all cut out, an initial current of about 0·03 amp. is obtained, which tends to rise considerably as the experiment goes on. Even 0·03 amp. is too large for very accurate work, on account of errors arising from diffusion accelerated by the heating effect of the current. When, however, it is not wished to pass the current longer than 1 hour, 0·03 amp. will have to be used to obtain a suitable volume of gas in the voltameter,

and this value can be maintained by varying **R**. Whilst it is desirable to use a small current passing for a long time rather than a larger current passing for a shorter time, there is, on the other hand, a limit to the smallness of the current and the length of the time. The most suitable current will of course depend on the dimensions of the transport-number vessel or vessels containing the liquid under investigation. Again, if the current is allowed to pass too long, diffusion effects will be observed. It is to be noted that with the present simple apparatus there is no experimental method of detecting any error due to diffusion. However, if 3 beakers are used in series having 2 connecting **Y** tubes, then there ought to be no change in the concentration of the liquid in the middle beaker.

After the current of 0·03 amp. has passed for 1 hour, bring the liquid in **B** to the same level as in **G**, and take readings on **B**, on the barometer and on the thermometer.

Let the readings be r_2, b and t. The volume of gas reduced to 0° and 760 mm. will be

$$v = (r_2 - r_1) \times \frac{b - h}{760} \times \frac{273}{273 + t}$$

where h = vapour pressure of $2n$ NaOH (about ·25 mm. < for water).

$\frac{22{\cdot}41 \times 10^3}{4}$ c.c. is one equivalent of oxygen

and $\frac{22{\cdot}41 \times 10^3}{2}$ c.c. is one equivalent of hydrogen;

therefore $\frac{22{\cdot}41 \times 10^3 \times 3}{4}$ c.c. is one equivalent of the gaseous mixture obtained in the voltameter. The number of c.c. obtained divided by $\frac{22{\cdot}41 \times 10^3 \times 3}{4}$ is the number of equivalents of ions liberated at any one electrode in the circuit as the result of passing the current. Let the number of equivalents $= x$. After breaking the current, open the stop-cock above **Y**, and allow it to empty into **X** and **Z**. Weigh the

solutions in **X** and **Z** and titrate with $\frac{n}{10}$ NaOH. Also titrate a weighed quantity of the original solution. Let the number of equivalents of H_2SO_4 in **X** after the experiment be a, and let the corresponding weight of water be w_1. Suppose that corresponding to w_1 grams of water there were originally b equivalents of H_2SO_4. Then a is greater than b, and increase in equivalents of SO_4 near anode $= a - b$. But if current were all conveyed by SO_4 increase would be x; therefore only the fraction $\frac{a-b}{x}$ of the electricity is conveyed by the SO_4 ions. In other words, $\frac{a-b}{x}$ = **transport number** for SO_4.

There is a fall in the number of equivalents of H_2SO_4 in the neighbourhood of the cathode. Let the number of equivalents of H_2SO_4 in **Z** after the experiment be c and the corresponding weight of water w_2, and suppose that for w_2 grams of water the original number of equivalents was d. Then $c < d$ and $d - c$ = fall in number of equivalents of SO_4 in the neighbourhood of the cathode. But if the electricity were all conveyed by the anions the fall would be x equivalents; therefore the fraction $\frac{d-c}{x}$ is conveyed by the SO_4 ions. In other words, $\frac{d-c}{x}$ is the transport number for the SO_4 ions. This number should equal $\frac{a-b}{x}$. Also $1 - \frac{a-b}{x}$ or $1 - \frac{d-c}{x}$ = **transport number** for the H ions.

The following is an account of a transport-number experiment, which, however, is unsuitable as an exercise if the available time is limited:

Determination of the Transport Numbers of the Silver Ion and the Nitrate Ion in a Solution of Silver Nitrate.

The apparatus (see Fig. 46) consists of a **Voltameter V**, a **Transport-Number Vessel** *T*, an Ammeter **M** and a Variable

Resistance **R**, arranged in series and supplied with current from terminals at a voltage of 30 to 40 volts. The Voltameter is as in the last experiment, and is used in the same way, or a copper voltameter may be used instead, consisting of two copper plates dipping in a solution containing 125 grams of $CuSO_4 \cdot 5H_2O$, 50 grams of concentrated H_2SO_4, 50 grams of alcohol and

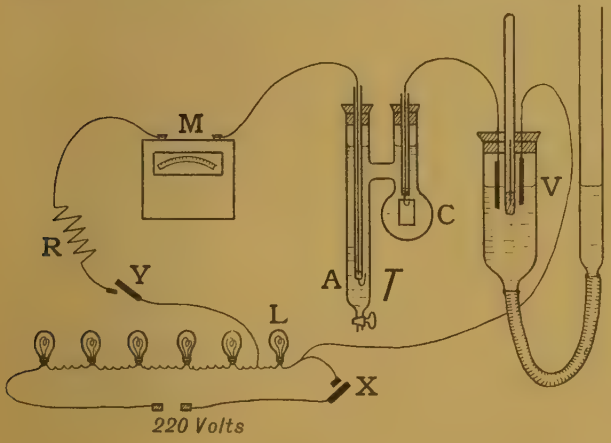

FIG. 46

1000 grams of water. In the copper coulometer the current density should be between 0·5 and 3 amps. per sq. dm.

In the Transport-Number Vessel the anode **A** is a silver wire, which should be freshly plated before the experiment, and the cathode is a silver plate. The plating of the silver anode wire may be carried out thus: Make the wire the cathode in an electrolytic cell containing a solution of potassium silver cyanide. Use a current density of 0·15 to 0·5 amp. per sq. dm. To get rid of occluded cyanide, make the wire first the anode, then the cathode, in a hydrochloric acid solution. The passing into solution of the silver of the anode wire is most marked at those parts of the anode nearest the cathode; therefore the end of the anode wire is turned upwards.

Fill the Transport-Number Vessel with $\frac{n}{20}$ silver nitrate solution; about 80 c.c. will be required. Fit up the apparatus as in Fig. 46.

Having taken the initial burette reading, complete the circuit. Between 0·01 and 0·015 ampère should be passed through the apparatus. To obtain the current, a voltage will be required whose value depends on the total resistance of the apparatus. To obtain the necessary fraction of the 220 volts, a number of lamps may be placed in series. For example, place six 16-candle-power carbon filament lamps in series across the 220 volts terminals of the lighting mains; then between the terminals of **L**, one of these lamps, there will be a potential difference of between 30 and 40 volts, before connecting the shunt circuit containing the apparatus. Connect the terminals of the apparatus to the terminals of **L**, inserting the switch **Y**.

With the main switch **X**, turn on the lighting circuit current through the lamps. With sub-switch **Y**, turn on the branch current through the apparatus. The voltage at the terminals of the lamp **L** is, of course, now reduced. Regulate with the variable resistance **R** until the current is between 0·01 and 0·015 ampère. Allow the current to pass 2 hours. In the meantime prepare 250 c.c. of $\frac{n}{20}$ NH_4CNS solution.

Titrate a weighed portion of the same $\frac{n}{20}$ $AgNO_3$ solution as was used to fill the Transport Vessel.

After the current has passed long enough level the burette, and take a reading on the burette, the thermometer and the barometer. Hence calculate the volume of the gaseous mixture liberated, reducing the volume to 0° and 760 mms., as in the last experiment.

$9{\cdot}650 \times 10^4$ coulombs correspond with $\frac{22{\cdot}41 \times 10^8 \times 3}{4}$ c.c. of the mixture. Therefore, the number of c.cs. of mixture liberated

divided by $\frac{22{\cdot}41 \times 10^3 \times 3}{4}$ give the number of equivalents discharged (or charged) at each electrode of the transport-number vessel. Let this number $= x$. If the copper coulometer is used, the cathode is weighed before and after passing the current, and the increase in weight divided by the equivalent of copper gives the number of equivalents discharged or charged at each electrode.

Run off $\frac{2}{3}$ of the liquid at the anode side of the migration vessel into a weighed flash E. This should contain all the liquid in the neighbourhood of the anode which is likely to have changed in composition owing to migration of the ions or to slight diffusion.

Run off what was the middle portion of the solution into a weighed flash F. There should be no change in the composition of this middle layer, unless bad manipulation (having too heavy a current and consequent heating or a current passing too long) leads to excessive diffusion.

Titrate the liquid in E with $\frac{n}{20}$ NH_4CNS, and let the weight of water $= w_1$ and the number of equivalents of $Ag = s_1$.

Titrate the liquid in F with $\frac{n}{20}$ NH_4CNS, and calculate the number of equivalents of silver there would be for a weight w_1 of water. Let this number $= s_2$.

From the titration of the original solution calculate the number of equivalents of silver there would be for a weight w_1 of water. Let this number $= s_3$.

Then $s_3 = s_2$ if the experiment has been properly carried out.

Since coulombs corresponding to x equivalents have passed through any cross section, x equivalents of silver have dissolved from the anode; therefore the anode liquid would be richer in silver by x equivalents if no silver migrated away from the neighbourhood of the anode. The anode liquid is actually richer by $s_1 - s_3$ equivalents of silver.

Therefore $x - (s_1 - s_3)$ equivalents are lost, owing to migration of the silver ions.

Thus, $\frac{x - (s_1 - s_3)}{x}$ is the fraction of the electricity conveyed by the silver ions or $\frac{x - (s_1 - s_3)}{x}$ is the transport number of the silver ion, and $\frac{s_1 - s_3}{x}$ is the transport number of the nitrate ion in the given solution of silver nitrate. The error allowable is $\pm 2\%$.

E. W. Washburn (*Jour. Amer. Chem. Soc. 31*, 330, 1909) describes a Transport-Number Vessel in which glass stop-cocks can be turned to separate the electrode liquids from the middle liquid. *The apparatus is of uniform bore throughout* (2·3 cms. diam.), *including the cross-tubes of the stop-cocks*; this is to prevent local heating and consequent stirring during the passage of the current. The apparatus was used to examine halogen acids and their salts.

CONDUCTIVITY OF ELECTROLYTES (INTRODUCTION).

ACCORDING to **Ohm's law** the current passing through an electrical conductor is equal to the difference of potential between the ends of the conductor divided by the resistance of the conductor

$$\text{or} \qquad \text{current} = \frac{\text{difference of potential}}{\text{resistance}}$$

$$\text{or} \qquad \text{ampères} = \frac{\text{volts}}{\text{ohms}}.$$

The International Ohm is the resistance offered at 0° to an unvarying current by a column of mercury 106·300 cms. long weighing 14·4521 grams and of constant cross section. E.M.F. of a Standard Weston cell = 1·0183 **International Volts** at 20°C.

According to the **theory of electrolytic dissociation,** when a substance called an **electrolyte** is dissolved in water, a fraction of the total weight of solute is in the solution in the form of **sub-molecules** or **ions** which are electrically charged, or it may be that practically all the solute is in this condition. The above mentioned fraction is called the **degree of dissociation**. The presence of the ions renders the solution a conductor.

If R = the resistance of a portion of the solution between (say) two parallel electrodes and c = the conductance of the same portion of solution, then $c = \frac{1}{R}$.

If $R = 5$ ohms, then $c = \frac{1}{5}$ or 0·2 **mho** or **reciprocal ohm**. If the parallel electrodes have each an area of 1 sq. cm. and are 1 cm. apart, then 5 ohms is the **specific resistance** or the

resistivity, and 0·2 mho or reciprocal ohm is the **specific conductance** or the **conductivity** of the given liquid, or $\kappa = 0{\cdot}2$. Thus the conductance c and the conductivity κ are not equal unless the electrodes have each an area of 1 sq. cm. and are 1 cm. apart. Usually this is not the case in an electrolytic cell. Thus, c is measured and κ has to be calculated. In a given cell the ratio $\frac{\kappa}{c}$ for one liquid is the same as for all other liquids.

The value of κ being already known for (say) $\frac{n}{50}$ KCl, the value of c for this liquid can be measured and the value of $\frac{\kappa}{c}$ for the cell calculated. $\frac{\kappa}{c}$ is called the **Cell Constant**; its value depends on the dimensions of the electrodes and their position relative to one another. Any change in either of these quantities would involve a change in the cell constant. **Current strength**, or simply **current**, is said to be 1 **ampère** when there passes through any cross section of the circuit, 1 **coulomb per second.**

Current density refers to a certain place in the circuit, and is the number of coulombs per second that pass through unit area of the cross section at that place. **Current density** may be different at different parts of the circuit; **current** is the same at all parts of the circuit. **Current density** at any point in the circuit is equal to the **current** divided by the area of the cross section at that point.

When the fall of potential is 1 volt for a distance of 1 cm., the conductivity $\kappa =$ the current density.

$\kappa = 9{\cdot}650 \times 10^4 \gamma\eta(U_A + U_c)$, where $U_A =$ velocity of migration of the anion when potential gradient $= 1$, and $U_c =$ velocity of migration of the cation when potential gradient $= 1$.

$\eta =$ number of gram equivalents of electrolyte in 1 c.c. of solution.

$\gamma =$ degree of dissociation, or that fraction of the total weight of electrolyte which is present in the form of ions.

Equivalent conductivity

$$= \Lambda = \frac{\kappa}{\eta} = \kappa v = 9{\cdot}650 \times 10^4 \times \gamma(U_A + U_c),$$

where v = the volume in c.c. occupied by one gram equivalent.

Molecular conductivity $= \mu = \frac{\kappa}{M} = \kappa V$, where V = volume occupied by one gram molecule and M = number of gram molecules per c.c.

For substances like KCl, where the ions are monovalent, $\Lambda = \mu$. Λ will be used here.

When the solution is diluted, during the progress of dilution γ increases to the limit 1 and η diminishes or v increases. When the **gram-equivalent volume** or the "**dilution**" is v, let the equivalent conductivity $= \Lambda_v$.

$$\Lambda_v = 9{\cdot}650 \times 10^4 \times \gamma(U_A + U_c)$$

and

$$\Lambda_\infty = 9{\cdot}650 \times 10^4 (U_A + U_c);$$

$$\therefore \frac{\Lambda_v}{\Lambda_\infty} = \gamma.$$

Put $\Lambda = l_A + l_c$,

where $l_A = 9{\cdot}650 \times 10^4 \times \gamma U_A$

and $l_c = 9{\cdot}650 \times 10^4 \times \gamma U_c$.

l_A and l_c are the ionic conductivities, and are different at different dilutions.

$$\frac{l_A}{l_c} = \frac{U_A}{U_c} = \frac{n_A}{n_c} = \text{ratio of Transport Numbers.}$$

Combining this equation with

$$l_A + l_c = \Lambda$$

we can calculate l_A and l_c.

The measurement of resistance in the case of electrolytes is more difficult than in the case of metallic conductors, on account of the phenomenon of **polarisation** which occurs at the surface of the electrodes dipping in the solution. A direct current sent through a solution of an electrolyte becomes weaker owing to the development of an opposing polarisation. The heavier

the original current the more marked is this change. Various methods have been devised to overcome this difficulty.

The following may be noted: (1) **A Wheatstone Bridge method** in which a direct current is used, and two cells different in size containing the electrolytic solution are placed in corresponding arms of the bridge, so that the polarisations balance one another. (2) **A Potentiometer** method. (3) **A Wheatstone Bridge method** in which an alternating current of high frequency is used.

The third method is the most common.

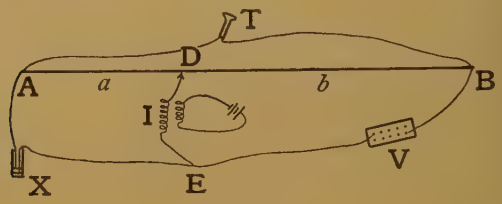

FIG. 47.

The apparatus is as in Fig. 47, which shows a **Wheatstone Bridge**. **I** is a small induction coil which sends out an alternating current which, for one of the directions of current-flow, enters the wire **AB** at the movable point of contact **D**, where it divides, part going along **DA** (length $= a$) and along through the electrolytic cell (resistance $= \mathbf{X}$) to **E** and back to **I**, and part going along **DB** (length $= b$) and along through the resistance box (resistance $= \mathbf{V}$) to **E** and back to **I**. When there is a balance no current passes through the telephone, and no sound is heard. (What is usually obtained in practice is not absolute silence but a sound minimum.) This balance occurs when $\mathbf{X} : \mathbf{V} = a : b$, that is when the points **A** and **B** are at the same potential. The connection with the source of current is made at **D** and **E** and not as is usual with a Bridge at **A** and **B**, because, when there is a tapping key at **D**, the current is passing only for the short time during which an observation is being made.

The less the current density, the less is the polarisation. Therefore, the electrodes in the cell are made of large area and are platinised. Also, a very small induction coil is used giving a feeble current, and having a very light hammer or trembler which vibrates very rapidly, giving an alternating current of high frequency, this last result tending still further to diminish the effect of polarisation. There is the additional advantage that a note of high pitch is easier to distinguish in the telephone than a note of low pitch.

FIG. 48.

The electrolytic cell usually consists of a Jena glass cylinder (see Fig. 48) provided with two **electrodes** in the form of platinum discs connected to platinum wires, which are fused through glass tubes held in position by an ebonite stopper which fits the Jena glass cylinder. The glass cylinder should be thoroughly steamed out before use. Mercury is put into the tubes, in which dip the wires connecting to the rest of the apparatus. Both electrodes are as large as convenient and are platinised, being coated by electrolysis with a black velvety deposit of platinum. The surface of a platinised electrode is several thousand times greater than that of the polished electrode. The current density is therefore much reduced and, as indicated above, the polarisation also.

Platinising of Electrodes.

This may be done by cleaning the electrodes with chromic acid mixture and placing in a solution containing 3 grams of chloroplatinic acid, 0·02–0·03 grams of lead acetate and 100 c.c. of water.

Place the electrodes in an inclined position, to allow gas to escape easily, and connect by means of a reversing switch with 2 accumulators. Continue the electrolysis for 15 minutes, reversing the current every half minute, so that the electrodes

act alternately as cathode. To free from substances absorbed by the **platinum black**, place the electrodes in a solution of dilute sulphuric acid and pass a current for half an hour, reversing every minute. Wash with warm CO_2-free water and, as should always be done when the electrodes are not in use, leave them immersed in CO_2-free water.

Even if thoroughly satisfactory results are desired, bright platinum electrodes may be used for conductances up to 0·0004 reciprocal ohm per sq. cm. of electrode surface, electrodes coated with platinum black up to 0·01 reciprocal ohm per sq. cm. and electrodes coated with palladium black up to 0·04 reciprocal ohm per sq. cm. In exceptional circumstances, when it is desired to use these electrodes for conductances beyond the above limits, the application may be extended with fair success in the first to 0·002 reciprocal ohm per sq. cm., in the second to 0·05 reciprocal ohm per sq. cm. and in the third to 0·2 reciprocal ohm per sq. cm. For example, when platinum black cannot be used on account of its catalytic action on the solution, bright platinum may be available, and when palladium is attacked by strong oxidising liquids platinum may have to be used. Conductance in this paragraph means conductance of the electrolyte cell.

Conductivity Water.

"**Conductivity water**" is water used in preparing solutions for experiments in electrolytic conductivity. Sometimes ordinary distilled water, owing to the presence of substances in solution, cannot serve as "conductivity water," which should not have a conductivity greater than 2 to 3×10^{-6} reciprocal ohms or 2 to 3 gemmhos. Purer water than this can be obtained, but under ordinary conditions (for example, in the ordinary form of electrolytic cell, which is not air-tight) it soon acquires a higher conductivity. To obtain conductivity water, heat with potassium permanganate solution containing a few drops of sulphuric acid. Distil, shake with caustic soda and redistil, using a glass condenser. Redistil, using a tin-tube condenser, and reject the first third and the last third of

distillate. The water should be stored in a bottle made of a sparingly soluble glass, such as Jena glass, or the bottle should be properly "seasoned." This precaution is necessary, because soluble matter in the glass passing into solution would add appreciably to the conductivity. If very accurate results are desired it is advisable to use freshly prepared conductivity water. By bubbling carbon-dioxide free air through the water, it may be further freed from carbon dioxide.

Water may be also improved for conductivity purposes by fractional solidification. The portion crystallising first is found to have its resistance raised.

For work with very dilute solutions it is necessary to use conductivity water having a conductivity of lower value than that mentioned above. Robert Bourdillon (*Journ. Chem. Soc.*, May 1913, page 791) describes "a still which will deliver 7 or 8 litres of water of conductivity below 0·2 gemmho in a single distillation from Oxford tap water." Potassium hydrogen sulphate is added to the original water and a vertical tin condenser (2·5 cms. internal diameter and 145 cms. long) is used, up which is blown a current of pure air. The air current removes volatile impurities. All the connections are kept air-tight, this being important when the distillation is carried out in a badly ventilated room. *Preparation of water of low conductivity is futile if the conductivity cell is not air-tight.* Bourdillon points out how slight is the rise of conductivity if a suitable cell is used, and also that water of a conductivity of 0·12 gemmho can be kept for a month or two in 3-litre Jena glass flasks with siphon outlet tubes and air inlets protected by soda-lime tubes, without its conductivity rising above 0·5 gemmho.

The Bridge Wire.

The bridge wire consists of a platinum, platinum-iridium, or constantan wire of uniform diameter, usually 1 meter long and 0·1 to 0·2 mm. in diameter. It is sometimes stretched along a

piece of wood having a scale graduated in millimetres. A sliding contact with a platinum edge acts as the movable contact. If a longer wire is desired, it would be inconvenient to fix it in this way, and so the wire is sometimes wound round a cylinder. For example, the bridge in one form of apparatus consists of a wire 2500 mms. long coiled round a cylinder with its axis placed vertically. The movable contact is changed by turning a screw at the top, and an indicator shows not only the values of a and b but also the value of the ratio $a : b$. This value multiplied by **V** gives the value of **X**.

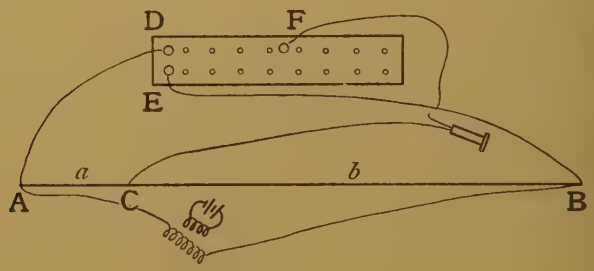

FIG. 49.

On account of wear, the wire should be calibrated from time to time. A standardised resistance box may be used. The box and the wire are arranged as a Wheatstone Bridge. (See Fig. 49.) One terminal **D** of the box is connected with one end **A** of the wire where the current may be made to enter, and the other terminal **E** with the other end **B** of the wire where the current leaves. An alternating current and a telephone may be used, the telephone being connected with the movable contact **C** of the wire and the movable terminal **F** of the box. Thus the two parts of the wire and the two parts of the box are the four arms of the Wheatstone Bridge.

Take out a 10 ohms plug from the box to form one arm and plugs corresponding to 990 ohms to form the other arm, and change the movable contact until the sound minimum is

obtained. The bridge reading should be 10. Let the actual reading be 9·9. This means that at this point on the wire, readings must be corrected by adding 0·1 to the actual readings.

The resistances obtainable from the box are

5000	2000	2000	1000	500	200	200	100
1	2	2	5	10	20	20	50

The following are examples of readings :

Arms of Box.				Correct Bridge Reading.	Actual Bridge Reading.	Correction
a		*b*				
10		500+200+200+50+20+20=990		10	9·9	+0·1
10+20= 30		500+200+200+50+20=970		30	29·9	+0·1
10+20+20= 50		500+200+200+50=950		50	50	±0·0
100		500+200+200=900		100	100·1	−0·1
100		200+200=400		200	200·2	−0·2
200+100=300		500+200=700		300	300·1	−0·1
200		200		500	500·1	−0·1
200+500=700		100+200=300		700	700	±0·0
200+200=400		100		800	800·1	−0·1
200+200+500=900		100		900	900·1	−0·1

Plot the corrections against the actual bridge readings, and to correct other readings use the curve thus obtained.

It is important in connection with conductivity measurements to bear in mind the influence of the following :

(1) Chiefly in the cell : **Temperature.**

(2) In any of the four arms of the bridge : **Polarisation, Self-induction** and **Electrostatic capacity.**

(1) The conductivity of an aqueous solution of an electrolyte might be said to increase by about 2 per cent. per degree. Therefore, if the temperature varies by $\frac{1}{20}$ of a degree, the conductivity varies by a $\frac{1}{20}$ of 2 per cent. or 0·1 per cent. The cell should be placed in a thermostat whose temperature variation is small enough to ensure this accuracy, and since the current in passing through the cell raises the temperature, the period of passage should be made as short as possible and the current as small as possible.

(2) In conductivity measurements by the telephone method, the aim should always be to obtain a sharp sound-minimum by adjusting the experimental details. A sharp sound-minimum implies that there are removed all inaccuracies that may have formerly been present owing to Polarisation, Self-induction, or Electrostatic capacity. Sometimes an attempt is made to obtain a sharp minimum by arranging the details of the bridge in as symmetrical a form as possible. Thus, polarisation in one arm may be balanced by a polarisation in the corresponding arm, and capacity in one arm by capacity in the corresponding arm.

Polarisation is reduced by making the frequency great and the resistance great; self-induction by making the frequency small and the resistance great; capacity by making the frequency small and the resistance small. Thus, conditions which favour the reduction of one effect may increase another, and a middle course must be followed in choosing the experimental details.

Polarisation. This exists in the liquid cells only. It can be got rid of almost entirely by using large electrodes, and by coating them with platinum black (or palladium black), and thus increasing their surface several thousand times, and diminishing very much the current density.

Self-induction. This exists chiefly in the coils of the resistance box, and may be diminished by bifilar winding of the wires of the coils. Any self-induction existing elsewhere in the apparatus can be easily removed, so that this effect should not give much trouble.

Capacity. This is chiefly seen in the bifilar wound resistance coils, especially those of high resistance. A higher resistance than about 500 ohms is therefore avoided.

The effect is also observable in cells of high resistance, and between the electrolytic cell and the water of the thermostat. This last capacity may be removed by using distilled water or by immersing the cell in petroleum contained in a beaker placed in the thermostat.

EXERCISE 32.

Determination of the Cell Constant.

If the electrodes have been freshly platinised, electrolytes absorbed by the platinum black and subsequently dissolved in the water of the cell would increase the conductivity, and must be removed.

To **test the purity of the electrodes,** put into the cell (see Fig. 48) rather more than enough conductivity water to cover the electrodes. Place the cell in a thermostat at 25°, and determine the resistance of the cell. It is important that the temperature of the cell should be kept constant. Pour out the water and put in fresh conductivity water, and measure the resistance. Repeat in this way until there is no change in the resistance, implying that the water is no longer dissolving matter from the electrodes. Thus a figure is obtained for the resistance of the cell when it contains conductivity water, from which the conductivity of the water can be calculated when the cell constant has been determined. The measurement of the resistance is carried out as follows.

Connect the electrodes of the cell with the rest of the apparatus by means of insulated heavy copper wires.

When the ends of the wires have to dip in mercury they should be immersed in dilute nitric acid, washed and then dipped in a solution of mercurous nitrate which amalgamates them. When the ends have to be fastened in binding screws, they should be cleaned with emery paper.

Connect the induction coil with two accumulators by means of a variable resistance and a switch. Make the other connections as in the figure.

Take out one or more plugs from the resistance box and start the coil by turning on the switch, plucking the hammer and, if necessary, moving the hammer-adjusting screw. Reduce the current as far as possible by changing the variable resistance. Place the coil at some distance from the telephone, so

that the sound heard through the telephone may not be masked by the sound heard directly from the coil. Move the sliding contact on the bridge-wire by turning the screw at the top of the cylinder until the sound becomes gradually fainter, passes through a minimum and then on further movement becomes gradually louder. Partly because the coils of the resistance box have either capacity or self-induction or have both, a position of absolute silence is not obtained, and a position is looked for, such that by moving the contact in either direction the sound is increased. Whenever a reading has been taken switch off the current.

The value of the resistance **V** of the resistance box suitable for conductivity water will depend on the size of the cell. Perhaps plugs will have to be taken out to give a resistance of 10,000 ohms.

Any error in reading the position of the sliding contact on the bridge wire has the least effect on the result at the middle point of the wire. On the other hand, the position of sound-minimum can be determined with greatest precision near the ends of the wire. Therefore a suitable position for the moving contact is (say) when the two parts of the wire are as 2 : 1.

Prepare a $\frac{n}{50}$ solution of potassium chloride, and rinse the electrodes and the cell repeatedly with this solution, and put into the cell more than enough of the solution to cover the electrodes. Determine the resistance as above at 25°. Repeat until a constant figure is obtained. If the resistance = 52·7 ohms, the conductance $= c = \frac{1}{52 \cdot 7}$ reciprocal ohm. $\kappa = 2 \cdot 765 \times 10^{-3}$, therefore the cell constant $= \frac{\kappa}{c} = \frac{2 \cdot 765 \times 10^{-3}}{\frac{1}{52 \cdot 7}} = \cdot 146$.

For *the specific conductivity* of $\frac{n}{50}$ potassium chloride solution at various temperatures see Table at the end of the book.

To enable the student to finish this experiment in one laboratory period, the apparatus should be fitted up beforehand.

EXERCISE 33.

Determination of the Equivalent Conductivity of Benzoic Acid and Calculation of its Degree of Ionisation at Various Concentrations.

Make a solution of exactly $\frac{n}{64}$ benzoic acid. Wash the electrodes repeatedly with conductivity water, and remove as much as possible of the water by holding filter paper against the edge of the discs. Finally, dry them by swinging them rapidly in the hot air above a hot plate heated (say) by a bunsen. Clean and dry the glass cylinder.

Pour exactly 20 c.c. of the $\frac{n}{64}$ benzoic acid into the cell, and place the cell in a thermostat at 25°. Put the electrodes into the solution, allowing no air bubbles to adhere to the surfaces of the discs. Also place in the thermostat a stoppered bottle containing conductivity water. When the temperature is steady, measure the resistance as above; hence calculate κ using the formula $\frac{\kappa}{\frac{1}{R}} =$ cell constant. Remove exactly 10 c.c. of the solution with a 10 c.c. withdrawal pipette, and add 10 c.c. of conductivity water with a 10 c.c. delivery pipette. Gently move the electrodes up and down until the solution and the water are thoroughly mixed. The solution is now $\frac{n}{128}$. Measure its conductivity. Repeat dilution and conductivity measurement until figures are obtained for $\frac{n}{256}$, $\frac{n}{512}$ and $\frac{n}{1024}$ solutions.

Thus the value of κ, the specific conductivity, is obtained for the various dilutions. Hence calculate the equivalent conductivity Λ_v for each dilution v; $\Lambda_v = \kappa v$ when $v =$ the **dilution** or the volume in c.c. occupied by an equivalent.

Λ_v increases as v increases to a maximum value Λ_∞. As shown above, the degree of dissociation at dilution v is $\frac{\Lambda_v}{\Lambda_\infty} = \gamma$.

Λ_∞ for benzoic acid = 381 at 25°. For the equilibrium $C_6H_5COOH \rightleftarrows C_6H_5COO' + H^\cdot$, by the law of mass action we have

$$\frac{(\text{concentration of } C_6H_5COO') \times (\text{concentration of } H^\cdot)}{\text{concentration of } C_6H_5COOH} = \text{a const.}$$

If 1 gram equivalent of acid is dissolved in v c.c. of solution, then the acid is present in the form of

γ gram molecules of C_6H_5COO',

γ gram molecules of $H^\cdot$

and $(1-\gamma)$ gram molecules of C_6H_5COOH.

Therefore, expressing the concentrations in molecules per c.c., we obtain

$$\frac{\frac{\gamma}{v} \times \frac{\gamma}{v}}{\frac{1-\gamma}{v}} \quad \text{or} \quad \frac{\gamma^2}{(1-\gamma)v} = K \quad \text{or} \quad \frac{\left(\frac{\Lambda_v}{\Lambda_\infty}\right)^2}{\left(1 - \frac{\Lambda_v}{\Lambda_\infty}\right)v} = K.^*$$

K is called **the "dissociation constant"** or **the "ionisation constant"** or **the "affinity constant"** of the acid.

Note that the unit of volume is here 1 c.c., not 1 litre, which is usually employed in calculating reaction constants.

Calculate the **"affinity constant"** for benzoic acid. The error should not be greater than ± 1 %. $K = 6 \times 10^{-5}$ for benzoic acid when v is expressed in litres.

When only one laboratory period is available for this experiment, different students should measure the conductivity for different solutions and compare results.

* Sometimes called Ostwald's **Dilution Law.**

ELECTROMOTIVE FORCE (INTRODUCTION).

We see in the study of **Faraday's Laws** the connection between the **amount of electricity** that has passed through any cross section of the circuit and the **amount of ions** liberated at each of the electrodes, and in the study of **Transport Numbers** we see how the conveying of the electricity is shared by the ions, but we have yet to see about the energy necessary to discharge the ions.

The work required to force a coulomb of electricity through a difference of potential of 1 volt is **1 joule**, or 1 joule = 1 volt-coulomb = 10^7 ergs. The number of joules required in any change is equal to the number of volts × number of coulombs. We already know one factor of electrical energy, namely the number of coulombs per equivalent of ions, and we have now to measure the other factor, namely the voltage or **electromotive force (E.M.F.)**.

When a metal dips in a solution of one of its salts, there is developed a difference of potential between the metal and the solution. A charged metallic ion present in the solution has to be forced through this difference of potential before it can be discharged and deposited on the cathode. There is, therefore, necessary an outside E.M.F. greater than the E.M.F. at the electrode and acting in the opposite direction.

The arrangement consisting of a metal dipping in a solution of one of its salts is called a **half-element**. The value of the E.M.F. of a half-element depends on the chemical nature and concentration of the metal in the electrode (for example

the concentration of the metal in an amalgam), and also on the chemical nature and concentration of the metallic ions of the solution.

The connection between ionic concentration and the E.M.F. of a half-element or "electrode," as it is sometimes called, is shown by the equation

$$E - E_0 = 2{\cdot}3026 \frac{RT}{nF} (\log_{10} C - \log_{10} C_0),$$

where E is the "**electrode potential**" or **E.M.F.** for ionic concentration C and E_0 that for ionic concentration C_0. If $C_0 = 1$, *i.e.* if the solution is of ionic normal concentration, then E_0, the corresponding E.M.F., is the so-called **Electro-Affinity**.

Hence $$E = E_0 + 2{\cdot}3026 \frac{RT}{nF} \log_{10} C,$$

where $R = 8{\cdot}32$ when electrical units are used,
T = the absolute temperature,
n = the valency of the ion,
F = one **faraday** ($9{\cdot}650 \times 10^4$ coulombs).

For ordinary temperatures (15° to 20°),

$$\frac{2{\cdot}3026 \times RT}{F} = 0{\cdot}058 \text{ approximately}$$

when electrical units are used.

Therefore $$E = E_0 + \frac{0{\cdot}058}{n} \log_{10} C.$$

The total concentration and the ionic concentration are usually not the same. Thus, even when it is possible to obtain a normal solution of a salt, it may be impossible to obtain an ionic normal solution; in such a case, the value of the electro-affinity must be calculated by extrapolation.

Two half-elements placed with their solutions in contact constitute a Galvanic cell, the metals of the half-elements being the poles of the cell. The E.M.F. of a complete element or cell is measured by comparison with the E.M.F. of a standard cell.

Standard Cells.

The standard usually employed is the **Weston Cell**, which may be represented thus :

$$Hg \mid Hg_2SO_4 \text{ (solid)}, \ CdSO_4 \text{ (saturated solution)},$$
$$CdSO_4\tfrac{8}{3}H_2O \text{ (solid)} \mid \text{Cd amalgam } (12\tfrac{1}{2}\% \text{ Cd}).$$

E.M.F. in International Volts

$$= 1{\cdot}0183 - 3{\cdot}8 \times 10^{-5}(t - 20^\circ) - 0{\cdot}65 \times 10^{-6}(t - 20^\circ).$$

Another well-known standard is the **Clark Cell**, which is

$$\dot{H}g \mid Hg_2SO_4 \text{ (solid)}, \ ZnSO_4 \text{ (saturated solution)},$$
$$ZnSO_47H_2O \text{ (solid)} \mid \text{Zn amalgam } (10\% \text{ Zn}).$$

E.M.F. in International Volts

$$= 1{\cdot}4325 - 1{\cdot}19 \times 10^{-3}(t - 15^\circ) - 0{\cdot}7 \times 10^{-5}(t - 15^\circ).$$

The amalgam percentages mentioned here are those usually employed, but are not entirely satisfactory (see below).

It will be seen that the composition of the two cells is similar, zinc in the Clark corresponding to cadmium in the Weston, and that temperature has a much greater influence on the E.M.F. of the Clark than on the E.M.F. of the Weston. Thus the Weston is now preferred to the Clark as a standard. In addition to a small temperature coefficient, it is important that the E.M.F. should remain steady when the temperature is constant. As mentioned above, the E.M.F. of any cell depends on the concentration of the electrolyte and the concentration of the electrode. The electrolytic solutions are saturated with respect to the solid salts in contact, and, therefore, provided these solids remain of constant composition, the aqueous solutions have always the same concentration for any given temperature. Within the range of temperatures for which the standards are used, there is not any difficulty in satisfying this requirement. Further, we must consider how the E.M.F. is affected by the composition of the amalgams constituting the anodes of the cells. Of the two amalgams, the one containing

zinc is the simpler. With excess of zinc, the amalgam consists of a liquid phase which is a saturated solution of zinc in mercury and a solid phase which is zinc only. Thus, for any given temperature we have, when there is excess of zinc, a solution of definite composition. The percentage of zinc in the saturated solution at 0° is 1·35, and with rising temperature increases to 2·85 at 39°. Within the usual range of temperatures, therefore, a 3 % amalgam would have an ample excess of zinc. This, however, gives too liquid a mixture; on the other hand, a 10 % amalgam, which it is the custom to use, is too hard. Hulett (*Physical Review*, vol. xxxii., March 1911) finds that a 7 % amalgam is sufficiently plastic at ordinary temperatures and most satisfactory.

According to Bijl (*Zeit. phys. Chem.*, *41*, 641, 1902) the cadmium amalgam is more complex. At 0° C. the saturated liquid solution contains 2·5 % of Cd, but when there is excess of cadmium the solid phase in equilibrium with 2·5 % liquid phase is not pure cadmium, but a 9 % solid solution of cadmium in mercury. An amalgam of total cadmium percentage below 2·5 consists of a liquid only, above 9 % it consists of solid only; an amalgam of total cadmium percentage anything between 2·5 and 9 % consists of a liquid phase (2·5 %) and a solid phase (9 %). Thus, even when the total cadmium percentage varies, (within certain limits) the liquid composition remains constant (and also the solid composition), and therefore the E.M.F. is not affected. Similarly, at 15° the total cadmium percentage may be anything between 4·4 % and 12 %. At 25° the limits are 5·6 % and 15 %, and at 35°, 7·1 % and 17 %. For ordinary temperature, then, the limits may provisionally be put down as 5 % and 15 %. For values below 10 %, however, the mixture is too liquid, and for values near the upper limit changes occur on heating from which the amalgam does not recover sufficiently rapidly on cooling. It is the custom to use 12½ %, but Cohen and Krypt (*Zeit. phys. Chem.*, *65*, 359) have shown that this % gives an unreliable cell below 14°. Hulett (*loc. cit.*) uses 10 %.

The Weston Cell may be constructed as follows:

An **H**-shaped vessel is taken with each side tube closed at the lower end, and having platinum wires fused through the closed ends. (See Fig. 50.)

A saturated solution of pure $3CdSO_4 \cdot 8H_2O$ is prepared, care being taken not to raise the temperature above 75°, because

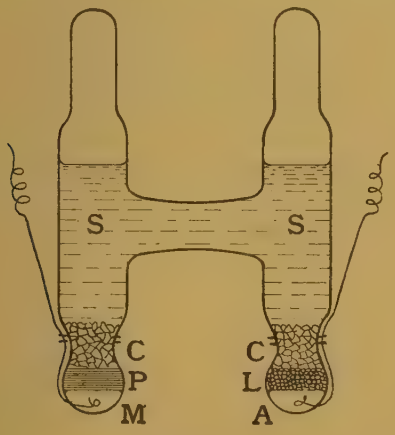

FIG. 50.

at this temperature there is a change from $3CdSO_4 \cdot 8H_2O$ to $CdSO_4 \cdot H_2O$.

In one limb of the **H**-shaped vessel is put a layer of pure mercury **M**, 1 cm. deep, and into the other limb a layer of cadmium amalgam **A**, 1 cm. deep.

To prepare the amalgam electrode, heat at 100° 7·0 parts of pure mercury and 1 part of pure cadmium. Stir well, keeping the temperature at 100°. Bring the **H** vessel to the same temperature and pour in the still liquid amalgam, which thickens on cooling. Hulett uses Hg : Cd = 9 : 1.

Above the mercury is placed a layer **P**, 5 mms. deep, of a paste made thus: Grind together mercurous sulphate, cadmium sulphate and a drop of mercury with a little saturated solution

of cadmium sulphate added. Filter through cotton wool. Rub paste again with cadmium sulphate solution and filter. Repeat till any mercuric sulphate present has been removed. Moisten the paste with a little saturated solution of cadmium sulphate and place above the mercury.

Above this paste is placed a layer of $3CdSO_4 \cdot 8H_2O$ crystals, **C**. At this point it is an advantage to have the tube constricted as in Fig. 50.

Above the amalgam is placed a layer **L**, 5 mms. deep, of finely powdered moist cadmium sulphate crystals. Above this is placed a layer of larger $3CdSO_4 \cdot 8H_2O$ crystals. At this point, the tube should be constricted as at the other side. The vessel is then filled to a point above the connecting cross-tube, with a solution **S**, saturated with regard to $3CdSO_4 \cdot 8H_2O$. On standing the cadmium sulphate crystals cake into plugs at the constricted parts of the tubes, and these plugs serve to keep in position the material below them.

In the open ends of the tubes is placed a layer of paraffin wax and then a disc of cork, which is completely covered with sealing wax. Air space is left between the paraffin wax and the liquid to allow for expansion. In some types sold by makers, the top is closed by fusing the glass tube itself. This form is shown in Fig. 50, and is sold by the Cambridge Scientific Instrument Co.

The International Committee, Jan. 1st, 1911, recommended as the E.M.F. of the Weston Normal Cell (12½ % Cd in amalgam), 1·0183 International Volts at 20° C. The temperature coefficient is very small; mean change in E.M.F. for the range 15° to 20° C. is −0·00004 volt for a rise of 1° C.

Standard Weston cells can be set up by different investigators with different materials which agree to within a few parts in 10^5.

When current has been allowed to pass through the cell, some of the solid Hg_2SO_4 goes into solution and effects recovery of the old E.M.F. The following shows the effect of short circuiting as found with a Weston cell:

Period of short circuiting	1 min.	5 min.	5 hours	5 days
Period required for complete recovery - -	40 min.	1½ hours	3 weeks	6 weeks

The Standard cell should be kept in an opaque case, so that the action of the light may not cause chemical change in the depolariser.

Measurement of E.M.F.

In one of the simplest forms of apparatus, 1 lead accumulator cell **E** (called the working cell, which should have a large capacity—50 ampère hours or over in order to have a steady voltage), a long wire **AD** (see Fig. 51) of uniform diameter

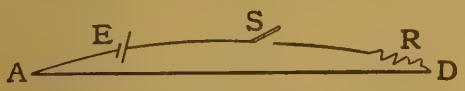

Fig. 51.

similar to that used in conductivity work, a regulating resistance **R** and a switch **S** are connected in series in one circuit. This is the **main circuit.**

When the main switch is on, with a uniform wire, the fall of potential along the wire will be regular. Therefore, the potential difference between any two points on this wire is proportional to the distance between these points.

Place in a small shunt circuit the Standard cell (say a Weston) **W**, connect the negative pole to the end **A** of the wire (see Fig. 52) and the positive pole through a two-way switch **T** and a galvanometer **G** to the sliding contact **B** on the wire. Turn **T** to connect **W** and **G**. Put on the main current, the negative pole of the accumulator being connected to **A**. Move **B** until there is no indication of current passing through **G**. This is obtained when the potential drop along the wire from **B** to **A** due to the working cell **E** is equal to the potential of the cell **W**.

Repeat with another cell **X** of unknown E.M.F., connecting the negative pole to **A** and positive pole through **T** and **G** to **C**. Put on main current, turn **T** to connect **X** and **G**, and move **C** until no current passes through **G**. Having thus obtained

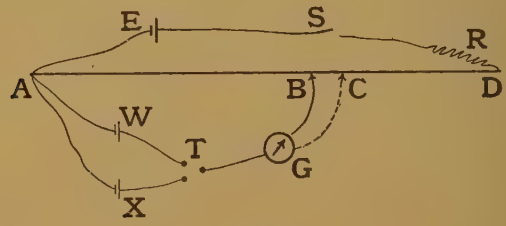

FIG. 52.

an approximate reading, repeat the whole experiment, comparing **W** and **X** more rapidly and accurately. Then

$$\frac{\text{E.M.F. of } \mathbf{X}}{\text{E.M.F. of } \mathbf{W}} = \frac{\text{length of } \mathbf{AC}}{\text{length of } \mathbf{AB}}.$$

This apparatus is called a **potentiometer**. The following is another method of using this instrument. Turn **T** to connect **W** and **G**. Set **B** at the reading on the wire, which has the same significant figures as the E.M.F. of the standard. Keep **B** fixed, and change the variable resistance until there is a balance. Now keep the variable resistance fixed, and turning **T** to connect **X** and **G** move **C** until there is a balance. Then the reading at the point **C** gives at once the significant figures of the E.M.F. of **X**.

Thus, if the E.M.F. of **W** were 1·0183 (**Weston**) and **B** were set at 10183, also if the reading at **C** were 14531, then the E.M.F. of **X** would be 1·4531.

To give greater accuracy of reading than can be obtained conveniently with the wire alone, there are sometimes introduced 14 other resistances connected in series with one another and with the wire, and equal to one another and to the wire. The main current passes through all the 15 equal resistances.

The number 15 is chosen, so that the instrument can be used by the second method with a Clark cell (E.M.F. 1·4325) if necessary.

The potentiometer with a wire and 14 resistances is graduated thus: The wire is laid alongside a scale divided into 1000 equal

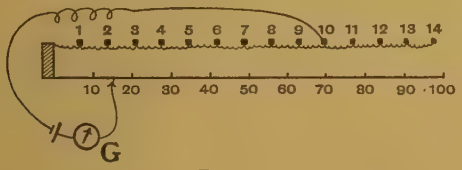

FIG. 53.

parts, the parts being numbered from the junction of the wire with the first of the 14 resistances, and the 14 resistances are numbered from the same place. Thus, when the instrument is set by the second method one pole of the Weston is connected to the plug number 10 (see Fig. 53) and the other pole to the sliding contact which is fixed at 183 on the wire. The total resistance between these two points is 10 resistances + 0·183 of a resistance or 10·183 resistances.

Capillary Electrometer.

To indicate the null point in E.M.F. measurements with the potentiometer, the **Lippmann Capillary Electrometer** (see Fig. 54) has been found more suitable than the Galvanometer.

The enclosed type of Capillary Electrometer is the most convenient and consists of two upright tubes **A** and **B** of about 5 mms. internal diameter placed parallel to one another. One of the tubes **B** ends at the bottom in a bulb; the other ends in a narrow capillary tube **C**, which is bent up to join the tube **B** about half way up. There is thus a narrow capillary passage connecting the two wide tubes. A small platinum wire is sealed through the foot of the bulb to serve as a terminal, which on the outside is soldered to a thin copper

wire. These wires are provided with a protecting tube, which may be filled with a soft viscous cement in which the wire lies best in the form of a spiral. A similar terminal is made near the foot of **A**, but projecting out horizontally. The bulb is about half-filled with pure mercury, and pure mercury is poured into the other tube until it stands about two-thirds up the capillary.

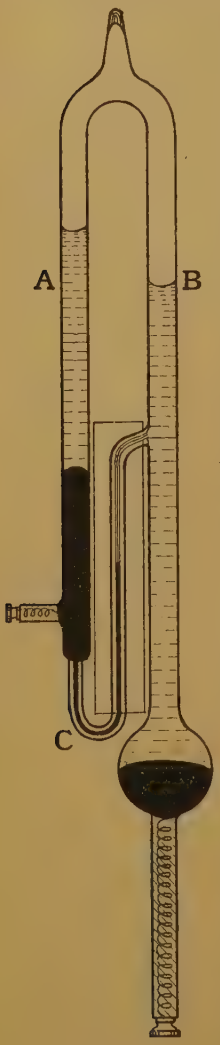

FIG. 54.

Boiled pure sulphuric acid of maximum conductivity is added. The two main tubes are either joined with a wide connecting tube or run into one tube at the top. In any case, the apparatus after the filling is pumped out and the glass sealed. The height of the mercury in the capillary may be adjusted by pouring mercury from one side to the other through the connecting cross-tube at the top. This instrument cannot lose any of its contents to the outside, nor can any impurity enter it from the outside; therefore its reliability is greatly increased.

If the mercury in the capillary is charged negatively, its surface will increase and it will travel up; if it is charged positively it will descend the capillary. This movement will be seen, then, if the bulb and the capillary are at different potentials. As far as possible it is arranged that current should always go through the electrometer in the direction from bulb to capillary, that is so that the capillary mercury rises. The other

direction is avoided as far as possible, because mercurous sulphate would be developed in the capillary.

The movement of the meniscus is followed with a microscope in the eye-piece of which is a scale. The instrument may be used for reading 0 to 0·9 volt, but is chiefly used for null work. Less than ·001 volt is detected. With the use of a microscope the movement due to ·0001 volt is appreciable. The bore of the capillary is elliptic, the longest axis of the ellipse being at right angles to the direction of vision. The glass capillary is illuminated by a small lamp behind, and has a thin glass plate cemented on in front in order to improve the sharpness of the image of the meniscus. The position of rest is obtained when the electrometer is short circuited on itself. A special key is employed which, when pressed down, puts the electrometer and the cell under study in series with one another, and when released short circuits the electrometer on itself. Therefore, on looking through the microscope and pressing down the key, one should see the mercury quickly moving, quickly to return to the position of rest whenever the key is released. When there is a movement it is better for the smooth working of the electrometer that the mercury should move up rather than down. If the meniscus moves, shift the movable contact until the position of rest is obtained.

A half-element may be built up in the following way: A small glass vessel about 11 cms. long and 2·5 cms. wide is closed at the bottom (see Fig. 55) and has two side-tubes **X** and **Y**. **X**, 2 to 3 mms. diam., entering near the bottom end of the vessel, is bent as in the figure and is narrowed at the end. In the top bend of **X** a tap is sometimes placed, which, when shut, keeps the solution in position and does not prevent the determination of the E.M.F.

Y is a straight tube, which enters near the top of the vessel. The vessel is closed at the top with a rubber cork, through which passes a straight glass tube **S**. Into the lower end of **S** is fixed with sealing wax a rod of the metal, to which is soldered

a copper wire which passes up the glass tube and acts as the terminal. There must be no part of the copper wire exposed to the solution. The narrow end of the bent side-tube **X** is dipped in the solution and the liquid sucked into the vessel by means of the straight side-tube **Y**, which is provided with rubber tubing and a clip. This clip is closed whenever enough liquid has been added. Then the end of the bent tube is removed from the stock of solution, and the electrode is ready for use.

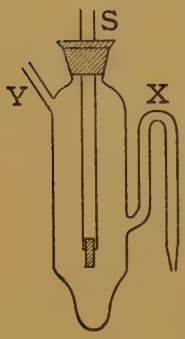

FIG. 55.

To construct a **gas electrode**, a vessel similar to that just described is used. In addition to **X** and **Y** there is a third tube **Z**, which after passing down parallel to the main vessel bends upwards, entering the vessel through a hole in the lower end. **S** is closed at the lower end, through which is fused a platinum wire to which is attached a piece of platinum foil. Platinise the foil as described under electrical conductivity, and to remove occluded chlorine leave the foil for half an hour in a solution of ferrous sulphate acidified with sulphuric acid. Then wash with distilled water and keep in distilled water until required. If a solution of (say) hydrochloric acid is placed in the vessel and if the foil is partly immersed in the solution, if also a slow stream of hydrogen is bubbled into the solution through **Z**, then a **hydrogen electrode** is obtained. If there is a definite pressure of hydrogen in the vessel, then the platinum black absorbs a definite amount of hydrogen. Corresponding to this and the hydrogen ions in the solution a definite E.M.F. is obtained. Thus the hydrogen gas takes the place of the usual metallic pole, the platinum merely serving as a medium. A **standard hydrogen electrode** is sometimes used in E.M.F. work instead of the calomel electrode mentioned below. As it takes rather long, unless the quantity of solution is small, for equilibrium to be established between

the gas and the solution when foil is used, there is sometimes substituted a long glass bulb coated with a thin film of platinum obtained by painting the glass with "liquid platinum" and burning on the platinum. Iridium, however, is to be preferred to platinum.

Two half-elements placed with their solutions in contact form a **Galvanic cell.** The metals of the half-elements are the poles of the cell.

For example, in the **Daniell cell** we have

Cu	Solution containing $Cu^{\cdot\cdot}$ ions (from $CuSO_4$)	Solution containing $Zn^{\cdot\cdot}$ ions (from $ZnSO_4$)	Zn.

Complete the circuit by connecting the copper and zinc with (say) a eureka wire.

In going round the circuit we find in passing along a wire or in passing through a solution that there is a gradual change of potential, but that there is a sudden change of potential at the surface of contact of two dissimilar materials, namely at the following places:

(1) Where two metals touch; where the copper and zinc meet the eureka.

(2) Where the two solutions meet.

(3) Where the copper meets its solution.

(4) Where the zinc meets its solution.

If in going round the circuit we agree to write as positive the value of a fall of potential, then we write as negative the value of a rise of potential.

When the temperature is constant, the E.M.F. due to contact between the metals vanishes. The E.M.F. between the leads of the cell is therefore equal to the algebraic sum of the two single electrode potentials (half-element E.M.F.S.) and the one liquid contact potential.

In studying the connection between E.M.F. and the chemical changes which occur at the electrodes, what is measured is the E.M.F. of the whole cell. Now, since this cell E.M.F. includes the liquid contact potential, a quantity which has nothing to

do with the electrode chemical changes but depends on differences between ionic migration velocities, it is necessary that the liquid contact potential should either be evaluated by calculation or eliminated by modification of the experimental details. The elimination may be effected either by adding to the two electrode solutions an indifferent electrolyte, for example, potassium chloride, or by dipping the bent tube of each electrode vessel in a saturated solution of potassium chloride, or potassium nitrate, or ammonium nitrate, this intermediate solution therefore serving to connect the two electrode solutions. When the liquid contact potential is thus eliminated, the cell E.M.F. is equal to the algebraic sum of the Single Electrode Potentials, or Half-element E.M.F.S.

If the contact potential is not eliminated, the cell E.M.F. is equal to the algebraic sum of the two single electrode potentials together with the liquid-contact potential value obtained as follows:

If two solutions of the same binary electrolyte are in contact, and the two ions are univalent, the liquid-contact potential

$$= \frac{l_c - l_A}{l_c + l_A} \frac{RT}{F} \log_e \frac{C_1}{C_2}$$

$$= \frac{l_c - l_A}{l_c + l_A} \times 2{\cdot}3026 \frac{RT}{F} \log_{10} \frac{C_1}{C_2},$$

where l_c and l_A are the ionic conductivities of the cation and the anion respectively.

With two solutions of different binary electrolytes, if all the ions are univalent and the ionic concentrations are equal, then the liquid-contact potential

$$= \frac{RT}{F} \log_e \frac{l_c + l_A'}{l_c' + l_A}$$

$$= 2{\cdot}3026 \frac{RT}{F} \log_{10} \frac{l_c + l_A'}{l_c' + l_A},$$

where l_c and l_A are the ionic conductivities for one electrolyte and l_c' and l_A' are the ionic conductivities for the other electrolyte.

Values of $2{\cdot}3026\,\frac{RT}{F}$ at 3 important temperatures:

Temperatures	0°	18°	25°
Values of $2{\cdot}3026\,\frac{RT}{F}$	0·0542	0·0577	0·0591

Thus, at 18° the concentration cell

$$\mathrm{Ag}\ \Big|\ \begin{matrix}\mathrm{Ag\,NO_3}\\ \text{concentration of } \mathrm{Ag^{\cdot}} = C_1\end{matrix}\ \Big|\ \begin{matrix}\mathrm{Ag\,NO_3}\\ \text{concentration of } \mathrm{Ag^{\cdot}} = C_2\end{matrix}\ \Big|\ \mathrm{Ag}$$

has the E.M.F.: $E_0 + 0{\cdot}0577 \log_{10} C_1 - (E_0 + 0{\cdot}0577 \log_{10} C_2)$ if the liquid-contact potential is not considered.

$$\text{The liquid-contact potential} = \frac{l_c - l_A}{l_c + l_A} \times 0{\cdot}0577 \log_{10} \frac{C_1}{C_2}.$$

$$\text{Total E.M.F.} = \left(1 - \frac{l_c - l_A}{l_c + l_A}\right) \times 0{\cdot}0577 \log_{10} \frac{C_1}{C_2}$$

$$= \frac{2l_A}{l_c + l_A} \times 0{\cdot}0577 \log_{10} \frac{C_1}{C_2}.$$

Measurement of Single Electrode Potentials.

To determine a single electrode potential, the unknown half-element and a half-element whose E.M.F. is known are put together to make a complete cell, the E.M.F. of which is determined. Hence, by subtraction, the unknown E.M.F. is calculated.

Preparation of Calomel Electrode.

The **Calomel Electrode** is sometimes used as a standard. This consists of mercury in contact with a saturated solution of mercurous chloride in a normal solution of potassium chloride (or decinormal). It may be constructed by the general method already described.

Prepare a normal solution of pure potassium chloride. Make a calomel paste by rubbing together in a mortar calomel and

mercury and a little of the normal potassium chloride solution. Wash two or three times by decantation with a little of the potassium chloride solution. Shake the rest of the potassium chloride solution with the paste to obtain a saturated solution of calomel. Put a little mercury into the electrode vessel (1 or 2 c.c.) and add a layer of calomel paste. Place the point of the bent side-tube **X** (see Fig. 55) under the surface of the potassium chloride solution saturated with calomel, and by sucking at the straight side-tube **Y** run the solution into the vessel. Close the clip and remove the point of the bent side-tube from the stock solution.

Connection with the mercury may be made by means either of a platinum wire passing through the wall of the vessel at the foot or of a platinum wire passing through the end of a closed glass tube which reaches down to the mercury layer and into which is poured a little mercury, by means of which connection is made to the outside.

In order that the E.M.F. of an electrode may be definite in its value, it is necessary that the electrode should be reversible and unpolarisable. If the value obtained by the null compensation method is independent of the direction in which the sliding contact is moved, then the electrode can be regarded as reversible and unpolarisable with the current employed in the measurement in approaching the equilibrium point.

The **absolute potential** (in volts) of the nKCl calomel electrode was found by the drop-electrode method (Rothmund, 1894) to be

$$+0{\cdot}5600+0{\cdot}0006(t^\circ-18^\circ)\pm0{\cdot}00005,$$

the mercury being positive to the solution. Sauer found that the potential of 0·1nKCl calomel electrode was greater than the potential of the 1·0nKCl calomel electrode by 0·051 at 18°.

It is considered more satisfactory, however, to work with **relative potentials**, a certain **reference electrode** being assumed to have zero potential.

The most important reference electrode is the **normal hydrogen electrode** or $Pt\,H_2 \mid H^+$, where the solution is

ionic normal with regard to $H^{\cdot}$ and where 760 mm. is the pressure (or partial pressure) of the hydrogen gas, *the reference electrode being supposed at the same temperature as the electrode under study.*

A potential measured in this way is written ϵ_h. When a cell, consisting of the given electrode and the normal hydrogen electrode, has for its positive pole the metal of the given electrode, then the value of ϵ_h is written with the positive sign.

It is the common practice to use the $1{\cdot}0n$KCl and the $0{\cdot}1n$KCl **calomel electrodes** as reference electrodes in measuring half-element potentials. It is most important, therefore, to know the values of ϵ_h for those reference electrodes.

Auerbach (*Zeit. für Elektrochemie*, 13-18, *18*, 1912) has shown by direct measurements at different temperatures that ϵ_h for the $0{\cdot}1n$KCl calomel electrode has the value $+0{\cdot}337$ from 0° to 30°. This is confirmed by a calculation from the Helmholtz equation, which shows that the temperature coefficient is zero.

The Helmholtz equation is

$$E = \frac{Q}{nF} + T\frac{dE}{dT},$$

where E = E.M.F. of the cell,

Q = heat of the reaction taking place in the cell,

T = absolute temperature,

$\frac{dE}{dT}$ = temperature coefficient,

and n and F have usual meanings. When Q is measured in calories, E is given in volts from $E = \frac{Q}{23063n} + T\frac{dE}{dT}$.

Using the above mentioned potential difference found by Sauer we see that ϵ_h for the $1{\cdot}0n$KCl calomel electrode has the value $+0{\cdot}286$ at 18°, and applying the Helmholtz equation we obtain the temperature coefficient.

Thus we have :

Electrode.		Values of ϵ_h at 0°	18°	25°
Hg	Hg_2Cl_2 0·1nKCl	+0·337	+0·337	+0·337
Hg	Hg_2Cl_2 1·0nKCl	+0·289	+0·286	+0·285

The "Potential Commission" of the German Bunsengesellschaft, 1911, have published values of ϵ_h at room temperature for electrodes in which the concentrations of the substances concerned in the electrode reactions are all molecular normal. The potential is then written ${}_0\epsilon_h$. See Table XIV.

In the case of a simple electrode such as Ag | Ag·, we have for any other concentration C of the ion Ag·

$$\epsilon_h = {}_0\epsilon_h + 0{\cdot}058 \log_{10} C \text{ at room temperature.}$$

It will be seen that E.M.F. measurements afford a convenient means of obtaining concentrations.

If ϵ_h' and ϵ_h are the potentials of the half-elements forming a cell, then the E.M.F. of the cell

$$= \epsilon_h' - \epsilon_h = {}_0\epsilon_h' + 0{\cdot}058 \log_{10} C' - ({}_0\epsilon_h + 0{\cdot}058 \log_{10} C)$$
$$= {}_0\epsilon_h' - {}_0\epsilon_h + 0{\cdot}058 \log_{10} \frac{C'}{C},$$

assuming that there is no liquid-contact potential.

If n = number of equivalents per ion,

then $$\epsilon_h = {}_0\epsilon_h + \frac{0{\cdot}058}{n} \log_{10} C.$$

Thus, for Zn | Zn··,

$$\epsilon_h = {}_0\epsilon_h + \frac{0{\cdot}058}{2} \log_{10} C.$$

If the 1·0nKCl calomel electrode is assumed to have zero potential and is used as a reference electrode, write the potential of the electrode under study thus : ϵ_c. When a cell, consisting of the given electrode and the 1·0nKCl calomel electrode, has for its positive pole the metal of the given electrode, then the value of ϵ_c is written with the positive sign.

Let the electrode Ag | $Ag^{\cdot}$ be measured against a 1·0nKCl calomel electrode at 18°, then the E.M.F. of the cell is ϵ_c and its value is written positive, Ag being the positive pole, current flowing outside the cell from Ag to Hg. But the 1·0nKCl calomel electrode is 0·286 volt above the n hydrogen electrode on the potential scale; therefore, for the given electrode,

$$\epsilon_h = \epsilon_c + 0{\cdot}286.$$

But
$$\epsilon_h = {}_0\epsilon_h + 0{\cdot}058 \log_{10} C;$$
$$\therefore\ \epsilon_c + 0{\cdot}286 = {}_0\epsilon_h + 0{\cdot}058 \log_{10} C.$$

Oxidation-Reduction Potential.

If an indifferent metal (*i.e.* not attacked) is immersed in a solution of reversibly interacting substances, an electrode potential is developed corresponding to the reaction at the electrode.

Let the reaction be

$$aA + bB = xX + yY,$$

where X and Y are in the higher state of oxidation, and let the substances have the concentrations [A], [B], [X] and [Y], then

$$\epsilon_h = {}_0\epsilon_h + \frac{RT}{nF} \log_e \frac{[X]^x\,[Y]^y}{[A]^a\,[B]^b}$$

or
$$\epsilon_h = {}_0\epsilon_h + \frac{0{\cdot}058}{n} \log_{10} \frac{[X]^x\,[Y]^y}{[A]^a\,[B]^b},$$

where ${}_0\epsilon_h$ is the normal potential or the value obtained when [A], [B], [X] and [Y] are each equal to 1.

${}_0\epsilon_h$ is the value given in the Potential Commission Table. n is the number of positive faradays acquired by X and Y during the change represented by going from left to right in the chemical equation.

This equation is analogous to

$$\epsilon_h = {}_0\epsilon_h + \frac{0{\cdot}058}{n} \log_{10} C,$$

for (say) Ag $Ag^{\cdot}$, C being the concentration of the substance in the higher state of oxidation, namely $Ag^{\cdot}$.

Affinity of a Reaction or the Change of Free Energy at Constant Temperature.

The affinity of a reaction occurring reversibly in a cell is

$$A = nFE \text{ volt-coulombs or joules}$$
$$= nFE \times 0{\cdot}239 \text{ calories}$$
$$= nE \times 96500 \times 0{\cdot}239 \text{ calories}$$
$$= nE \times 23063 \text{ calories},$$

where E = E.M.F. of the cell in volts and n = the number of faradays which pass through any cross-section of the circuit during the transformation of the gram molecules represented in the equation. For example, in

$$aA + bB = xX + yY,$$

n faradays correspond to a transformation of a gram molecules of A and b gram molecules of B to form x gram molecules of X and y gram molecules of Y.

EXERCISE 34.

E.M.F. of Half-elements.

Construct the half-elements

$$(1)\ \text{Cu} \mid \frac{n}{10}\,\text{CuSO}_4,$$

$$(2)\ \text{Zn} \mid \frac{n}{10}\,\text{ZnSO}_4$$

and form the cells

$$\text{Cu} \mid \frac{n}{10}\,\text{CuSO}_4 \mid \text{saturated KCl} \mid \frac{\text{Hg}_2\text{Cl}_2}{n\text{KCl}} \mid \text{Hg},$$

$$\text{Zn} \mid \frac{n}{10}\,\text{ZnSO}_4 \mid \text{saturated KCl} \mid \frac{\text{Hg}_2\text{Cl}_2}{n\text{KCl}} \mid \text{Hg},$$

and measure their E.M.F.

Hence calculate the E.M.F. of the half-elements.

Coat the copper pole electrolytically with copper, using a very small current density, and a solution containing 125 grams of $CuSO_4 \cdot 5H_2O$, 50 grams of concentrated H_2SO_4, 50 grams of alcohol and 1000 grams of water (**Oettel solution**). When

the metal, as in the case of zinc, is less noble than mercury, a second general method of treatment may usually be adopted. An amalgam is formed by rubbing mercury on the zinc rod. (The E.M.F. for saturated solutions of these metals in mercury is usually the same as that for the pure metal.)

In taking a measurement, the positive pole of the working cell and the positive pole of the unknown cell should be connected to the same end of the potentiometer wire. When it is not known which is the positive pole of a cell, it may be that the cell is at first connected up in the wrong way. If this is the case, it will be found impossible to obtain a balance until the poles are reversed.

Place the whole cell, including the intermediate vessel, in a thermostat at 18°.

Allowable error in E.M.F. is ± ·001 volt.

EXERCISE 35.

Study of a Concentration Cell.

Connect the apparatus as in Fig. 56, in which *V* is a voltmeter which reads to 120 millivolts and has a resistance of 500 ohms.

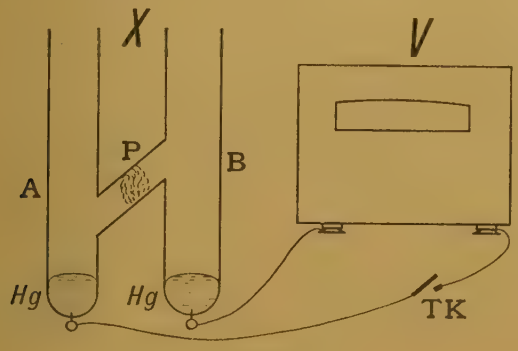

FIG. 56.

Into the limbs **A** and **B** of the vessel *X*, pour enough mercury to cover the platinum terminals. Into the cross-tube put a

plug of glass wool **P**. Into **A** and **B** pour a saturated solution of mercurous nitrate until the surface of the liquid reaches the upper end of the cross-tube. Use the tapping key **TK**, and look out for an indication of difference of potential between the electrodes in **A** and **B** by observing the needle of the voltmeter *V*. No movement of the needle is observed. Into **A** pour a saturated solution of potassium chloride and into **B** enough mercurous nitrate solution to keep the levels the same in **A** and **B**. Mercurous chloride is precipitated in **A**, and the concentration of the mercurous ion in **A** becomes less than that in **B**, and a difference of potential is indicated on *V* when **TK** is tapped. If the precipitate of mercurous chloride is allowed to fall and cover the mercury in **A**, the E.M.F. is reduced, but is restored again if the mixture in **A** is stirred.

EXERCISE 36.

Determination of Decomposition Potentials of n HCl, n HBr and n HI.

In the beaker **B** (see Fig. 57) (which is about 250 c.c. capacity, height $3\frac{1}{2}$ ins. and diam. $1\frac{1}{2}$ ins.) place about 155 c.c. *n* HCl, in which immerse the electrode **D** (platinised platinum wire) and the electrode **E** (platinised platinum plate) and the glass inverted thistle stirrer **T**. Connect the pulley **P** of the stirrer by means of a small rubber band with a 4 volts electromotor **M** clamped to a heavy iron stand. The speed of **M** is regulated by varying the resistance **F**, which is in the circuit containing the cells **G**, the switch **Y** and the motor **M**. By means of the switch **X** a current is sent through the resistance *R* from the two cells **C** which are placed in series. The main current passing through *R* is tapped at the points where the sliding contacts S_1 and S_2 touch *R*. The shunt current is sent through the milliammeter **A**, which reads up to 10 milliamps., and it enters the solution at the electrode **D**, leaving at the

electrode **E**. By means of **V** (reading to 2·5 volts) the voltage is measured at which the shunt current is supplied.

Start the stirrer **T**, regulating its speed with **F**. Slide $\mathbf{S}_1$ and $\mathbf{S}_2$ to the right, and with **X** send current through *R*. Slide $\mathbf{S}_1$ and $\mathbf{S}_2$ to the left, taking simultaneous readings on **V** and **A**, waiting until the current is steady before reading the milliam-

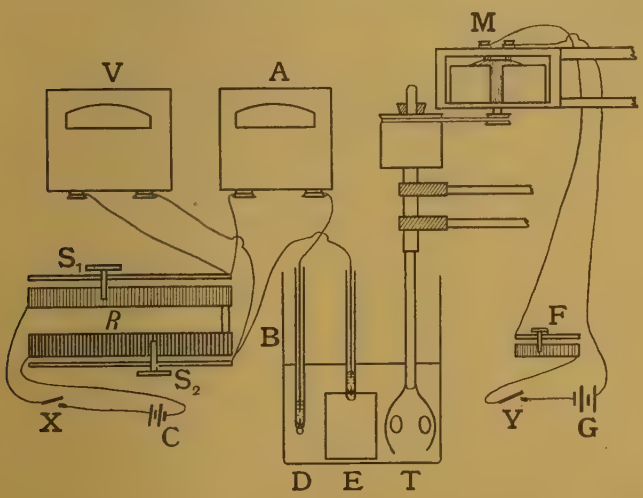

FIG. 57.

meter. Try the effect of stopping the stirrer. It will be observed that the current is reduced. This is due to the action of the back E.M.F. arising from concentration changes in the decomposition cell. The object of the stirring is to render the concentration as uniform as possible throughout the liquid and thus to reduce the back E.M.F. Keeping the stirrer in action raise the voltage in steps of ·05 volt, and plot the corresponding ammeter readings against the voltmeter readings. Observe that at a certain point there is a sudden increase in the current value. The corresponding voltage is the **decomposition potential** of *n* HCl, which is about 1·31.

In order better to ascertain the turning point in the curve, the plotting is carried out for some distance beyond this point. When about 1·6 volts is reached, stop the stirring and reduce the voltage until the ammeter reads zero, the applied voltage then exactly balances the back E.M.F. of the decomposition cell, and the voltmeter reading is the decomposition potential. Thus the value obtained by the first method can be checked.

Raise the applied voltage again above the decomposition value. By means of **X** switch off the current from **C**. A positive reading is still obtained on **V**, but a negative reading on **A**. The decomposition cell is, thus, a **secondary cell** or a **storage cell**, having been charged by the current from **C**. The readings on **V** and **A**, however, quickly fall to very low values, so that the decomposition cell is a storage cell of very **low capacity**.

The **decomposition potential** for *n*HBr can be determined by placing in the beaker containing the *n*HCl enough solid KBr to give a solution of HBr of the required strength. Start the stirrer, and when the KBr is dissolved proceed as before. About 0·94 volt is obtained. In the same way determine the value for *n*HI, which is about 0·52.

EXERCISE 37.

Determination of Cathode Over-voltage for Copper and for Lead.

Substituting a voltmeter reading to, say, 5 volts, but otherwise with the same apparatus as used to determine the decomposition potential of *n*HCl, determine the decomposition potential of 0·1*n*NaOH

(1) with platinised platinum plate as anode and platinised platinum plate as cathode;

(2) with platinised platinum plate as anode and copper plate as cathode;

(3) with platinised platinum plate as anode and lead plate as cathode.

The volt-amp. curve shows the **decomposition potential** in (2) to be about ·25 volt higher than in (1), and in (3) to be about ·65 volt higher than in (1). These differences are the **cathodic over-voltages** for copper and lead relative to platinised platinum. Before visible evolution of gas is obtained, the voltage can be raised by these amounts higher in the cases of copper and lead than in the case of platinised platinum. This property is made use of in the electrolytic reduction of chemical compounds, where it is desired to raise the applied voltage as high as possible. By the use of a cathode, such as pure lead, having a high cathodic over-voltage, **electrolytic reductions** may sometimes be effected not otherwise obtainable. Similarly, **high anodic over-voltages** are taken advantage of in carrying out **electrolytic oxidations.**

It is to be noted that the values of the decomposition potential obtained by the volt-ampere curve method and by the zero-current method agree fairly well in the case of platinised platinum, but not in the cases of copper and lead, both of which show by the second method a value about 1·1 volts lower than that obtained by the first method, which yields the correct over-voltage. This implies that the back E.M.F. is more persistent with platinised platinum than with copper and lead.

EXERCISE 38.

Influence of a Depolariser on the E.M.F. of Ordinary Cells.

The apparatus is as in Fig. 58. **Z** is a rod of zinc (amalgamated on the surface) and **P** is a plate of platinum, **Z** and **P** are supported from rubber corks closing the limbs of *X*, which are connected with 3 cross-tubes.

In the cork to the right are other two holes, one through which passes the tube of the dropping funnel **F**, and another through which gas can escape and be led away and collected if required. From **F**, run in a dilute solution of H_2SO_4 (2*n*).

A cell is now formed consisting of a zinc electrode (anode) and a platinum electrode (cathode), each dipping in H_2SO_4. When **Z** and **P** are short circuited by dipping the wire **W** in the mercury contacts of *K*, then **Z** dissolves in the H_2SO_4 and hydrogen is evolved at **P** in fairly large bubbles. Remove **W**, thus leaving only the voltmeter *V* between **P** and **Z**. The reading is about ·7 volt. Replace **W** and leave the cell short circuited for about 15 minutes, and again remove **W**. Reading is now about ·65 volt.

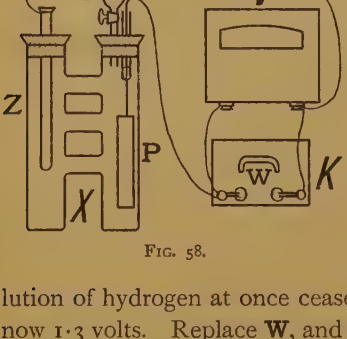

FIG. 58.

Replace **W**.

From **F**, run in a strong solution of CrO_3 (1 : 1). Evolution of hydrogen at once ceases. Remove **W**, and reading is now 1·3 volts. Replace **W**, and leave the cell short circuited for 2 hours. Remove **W**. Reading is still 1·3 volts. Replace **W**, and if the cell is left short circuited long enough the voltage will be observed to fall. This occurs when all the oxidising agent (CrO_3) is used up. Thus the effect of the depolariser (CrO_3) is to oxidise the hydrogen ions at the cathode, and thus to destroy the polarisation. A new and higher E.M.F. is developed, the value of which depends on the process of oxidation and reduction that is taking place at the cathode, and on the process occurring at the anode.

If a mixture of $K_2Cr_2O_7$, H_2SO_4 and water is used instead of a solution of CrO_3, then a voltage of 1·9 is obtained, which is the voltage of the ordinary dichromate cell. This cell may be constructed as follows: In a porous porcelain cylinder place a rod of carbon (used instead of platinum) and a solution of sodium dichromate (prèferable to potassium dichromate, since there is no crystallising out of chromium salt), concentrated sulphuric acid and water (12 : 25 : 100). Immerse the porcelain

cylinder in a glass jar in which is placed a dilute solution of sulphuric acid in which dips a rod of zinc. This may be taken as a type of the cells most commonly used. The following may be noted:

Anode.	Electrolyte.	Diaphragm.	Depolariser.	Cathode.	Name of Cell.	Voltage.
Zn |	H_2SO_4	||	Chromic acid	| Pt (or C)	*Dichromate*	1·9
Zn |	H_2SO_4	||	HNO_3	| Pt (or C)	*Grove* or *Bunsen*	2·0
Zn |	NH_4Cl solution	||	MnO_2 (solid)	| C	*Leclanché* also "*Dry cells*" in which electrolyte is absorbed by some porous material.	1·5
Zn |	$ZnSO_4$ (dil.)	||	$CuSO_4$ (concd.)	| Cu	*Daniell*	1·09
Zn |	alkali	||	CuO (solid)	| Cu	*Cupron*	1·0 to 1·1
Cd amalgam ($12\frac{1}{2}$ % Cd)	$CdSO_4\frac{8}{3}H_2O$ (solid) | $CdSO_4$ (in solution)	||	Hg_2SO_4 (solid)	| Hg	*Weston*	1·0183 at 20°
Zn amalgam (10 % Zn)	$ZnSO_4 7H_2O$ (solid) | $ZnSO_4$ (in solution)	||	Hg_2SO_4 (solid)	| Hg	*Clark*	1·4325 at 15°

In the cases where the depolariser is a solid the diaphragm may not be necessary.

Similarly for the lead accumulator or secondary cell.

Pb |	H_2SO_4, specific gravity 1·18, saturated with $PbSO_4$	||	PbO_2 solid	| Pb	*Lead accumulator*	2·05

EXERCISE 39.

Experiment to show Mass Action.

Study of $NaCl + HNO_3 \rightleftarrows NaNO_3 + HCl$. (1) This reaction may be made complete in the direction from left to right by keeping hydrogen nitrate in excess and removing hydrogen chloride as it is formed. (2) The reaction may be made

complete in the direction from right to left by keeping hydrogen chloride in excess and removing hydrogen nitrate as it is formed.

(1) Into a small weighed porcelain crucible weigh about 0·25 gram of dry sodium chloride. Let the weight of sodium chloride $= w_1$. Place an asbestos ring in a large porcelain crucible, and place the small crucible in the hole in the ring. Add some hydrogen nitrate (concd.) to the inner crucible. Heat the outer crucible until dryness is reached in the inner crucible, and weigh.

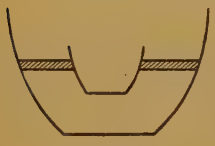

FIG. 59.

Add more hydrogen nitrate, heat and weigh again. Repeat the whole operation until the weight is constant. Let the weight of the solid in crucible $= w_2$.

(2) Now add some concentrated hydrogen chloride, heat and weigh, add more concentrated hydrogen chloride, heat and weigh again, and so on repeatedly until the weight is constant. Let the weight of solid in crucible $= w_3$.

It will be found that $w_3 = w_1$

and $$\frac{w_1}{w_2} = \frac{\text{molecular weight of sodium chloride}}{\text{molecular weight of sodium nitrate}}.$$

The chemical change in (1) serves as an illustration of Mass Action, because the hydrogen chloride is being continually removed from the field of activity which we are studying. We are not concerned with *how* it is removed. The removal is effected partly by the chemical interaction between the hydrogen nitrate and the hydrogen chloride and partly by diffusion. We keep adding hydrogen nitrate, and thus far more than make up for any loss of hydrogen nitrate, due to the interaction just mentioned. The important fact is that the hydrogen nitrate is present in large quantity, but the hydrogen chloride is prevented from acting effectively by its mass being kept low.

Similar remarks may be made regarding the reaction in (2).

PURIFICATION OF MERCURY.

Of impurities, metals cause the most trouble when we try to obtain pure mercury. The complete separation of metallic impurities may sometimes be effected by a chemical process followed by distillation. The chemical part of the purification depends on the fact that mercury is displaced from its solution by baser metals. If, therefore, a metal such as zinc is present in the mercury, then when the impure mercury is in contact, for example, with a nitric acid solution of mercurous nitrate, some zinc passes into solution a corresponding amount of mercury coming out of solution; this goes on until equilibrium is established, when some of the zinc will still remain in the mercury. Thus, even with strongly electropositive metals, complete separation of the metallic impurity cannot be brought about by this method, which should, nevertheless, be applied in order to have the mercury as pure as possible before starting the distillation.

If the mercury is very impure proceed thus: (1) Shake it vigorously in a separating funnel with a 5% solution of mercurous nitrate to which is added nitric acid to prevent precipitation of basic mercurous nitrate. At the earlier stages of this treatment open the stopper from time to time to equalise the outside and inside pressures. It should not be necessary to prolong the shaking beyond half an hour.

(2) Run off the lower layer into a second separating funnel and shake with distilled water.

(3) Run off the lower layer, dry the mercury with a hardened filter paper and filter through a filter paper (hardened) having

a small pin-hole in the apex of the cone. The mercury will now be separated from moisture, solids and some of the metals.

Fig. 60.

Dry mercury may also be obtained by varying the above procedure after the first shaking and adopting a method whereby, at the same time, the purification from metals is carried a stage further. Make use of an apparatus (see Fig. 60) consisting of a tube about 730 mms. long and 23 mms. in diameter, and ending at the foot in a capillary tube of 1 mm. bore, which is bent up as shown in the figure. Into the capillary pour pure mercury, and then add a solution of mercurous nitrate acidified with nitric acid, almost filling the wide tube. At the top is placed a funnel, the tube of which is pulled out to a narrow point and bent to the side, so that mercury poured into the funnel separates into small drops which describe a spiral path as they descend through the long column of liquid. During the descent the impure mercury is further purified according to the reaction above mentioned, and mercury comes out dry at the end of the capillary.

After use, the chemicals should not be allowed to stand in the apparatus, which should be cleaned out with nitric acid and dried. If the tube is fixed permanently to a stand, the cleaning may be simplified by having a tube containing a tap fused on to the lower bend of the capillary.

To complete the separation of metallic impurities, distillation is necessary. The boiling can be made to proceed smoothly if the gases present in the amalgam are completely removed, and the distillation is thus carried out in a vacuum. Hulett, however, in his investigations

on the distillation of amalgams (*Physical Review*, Oct. 1911), finds that the separation of metallic impurities by this method is very troublesome. For almost complete separation of **silver**, **gold** or **the platinum metals**, the amalgams would require two or three distillations, silver being the most difficult to remove. None of these metals, however, can be entirely removed from the mercury. Further, the difficulty is still greater with metals which have higher vapour pressures and very low melting points and boiling points, as for example with **zinc**, **cadmium**, **lead**, **tin** and **bismuth**, for the almost complete separation of which many distillations would be required in a vacuum or a reducing atmosphere. Hulett found, however, that all oxidisable metals can be removed by a single distillation in a current of air which is introduced into the distillation flash through the very narrow end of a tube which dips in the amalgam, a stream of small bubbles of air passing up through the liquid into the mercury vapour. Also, with this arrangement the boiling is free from bumping. The apparatus shown in Fig. 61 is essentially that described by Hulett. To construct the apparatus proceed thus: Ordinary round-bottomed distilling flasks with straight side-tube and neck about 130 mms. long will be found in most laboratories. Take one of these and draw out **B**, the top of the neck **N**, and fuse on a narrower tube **K**, which extends from **B** to **J** in the figure, and is about 150 mms. long. Take a glass tube **G**, which fits closely inside **K** and is about 470 mms. long, and drawn out at one end to a capillary. Place **G** with the narrow end dipping in the mercury, as shown in the figure. Make the apparatus air-tight at **J** by means of a rubber band which grips both **G** and **K**. Close the top end of **G** by means of a short rubber tube provided with a screw-clip **C**, and for the easier opening of this valve hang a small piece of copper wire inside the rubber tube. To the straight side-tube of the flask, fuse a tube 700 mms. long and near the flask bend the side-tube as shown in the figure. Pass the end of the side-tube through a rubber cork into the round-bottomed flask **R**, the side-tube **H**

of which is connected to a water-pump (or preferably to a mercury pump). Between **H** and the water-pump connect the flask **E**, the **U**-tube **U** and a pressure gauge and a tube containing calcium chloride. **E** is a safety-flask and **U** contains a

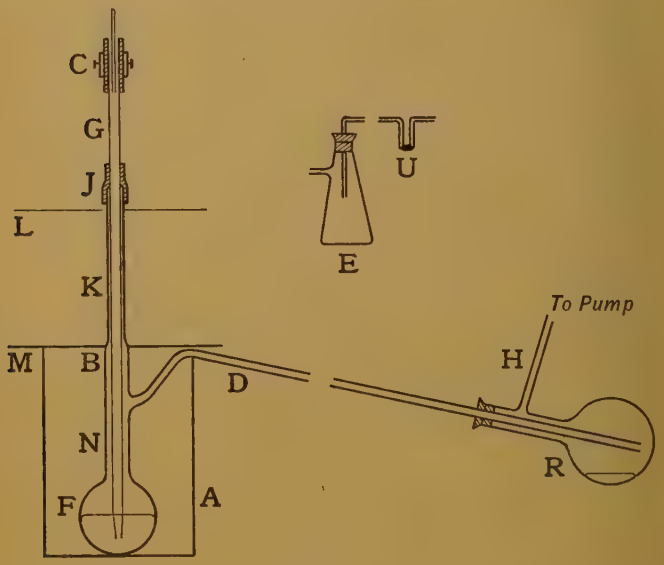

Fig. 61.

little mercury to indicate the rate at which air is being drawn through the apparatus.

Place the distilling flash in the asbestos air-bath **A**, and place the asbestos shields **L** and **M** to protect the rubber band at **J** and the upper part of the apparatus from the hot gases. Start the pump, heat the flask and regulate with the flame and **C**, so that the mercury vapour condenses at about **D**.

The most suitable conditions are a pressure of about 25 mms. with a corresponding temperature of 200° C. The partial pressure of the oxygen would then be about 5 mms. Thus, what happens will depend on whether the dissociation pressure

of a metallic oxide is less or greater than 5 mms. at 200° C. **If the dissociation pressure is less than 5 mms.** the oxide is formed: this is the case with all readily oxidisable metals, such as **zinc, cadmium, bismuth, tin, copper, lead,** etc., which are oxidised during the distillation, the oxidation taking place chiefly in the vapour phase and the oxide collecting in the distillate, which assumes a very dirty appearance if much impurity is present. The scum, however, can be readily removed by filtration through a pin-hole in a filter paper; and thus, under proper conditions, mercury is obtained free from the easily oxidisable metals.

On the other hand, **if the dissociation pressure of a metallic oxide is greater than 5 mms.** the oxide is not formed, the metallic vapour passes over and the metal collects in the distillate. This is the case with **mercury** itself and also with the nobler metals, such as **silver, gold** and **platinum metals.** It is, therefore, impossible by distillation to separate mercury completely from these metals. The distillate will always be a mixture of mercury and the metallic impurity in the proportion of the partial pressures of the metallic vapours in the distilling flask. The vapour pressures of pure silver, gold and the platinum metals at 200° are comparatively small, and when the metals are dissolved in mercury the partial vapour pressures are still smaller, so that distillation will greatly reduce the proportion of impurity. The separation, however, is never complete, and the presence of even small traces of metallic impurity has a marked effect on the properties of mercury.

TABLE I.

P is the probability that an error will be between $+x$ and $-x$. Instead of x, there are given $\frac{x}{\mathbf{p}}$ and $\mathbf{h}x$, where **p** is the limit of the range the probability of which is $\frac{1}{2}$ and where **h** is the constant of the probability equation for errors. See Burgess (*Trans. Roy. Soc. Edin.*, 1900) for corresponding values of $\mathbf{h}x$ and **P** (He writes t instead of $\mathbf{h}x$). The values in the present table were obtained by using the relation $\mathbf{h}x = \frac{x}{\mathbf{p}} \times \cdot 4769$ and rounding off the values of **P** given by Burgess.

$\frac{x}{\mathbf{p}}$	$\mathbf{h}x$	**P**	$\frac{x}{\mathbf{p}}$	$\mathbf{h}x$	**P**
1	0·4769	·5	4·088	1·949	·9941
2·63	1·254	·9238	4·1	1·955	·9943
2·890	1·378	·9487	4·2	2·0030	·9954
3·0	1·4307	·9570	4·254	2·029	·9959
3·05	1·4545	·9603	4·3	2·052	·9963
3·1	1·4784	·9634	4·4	2·098	·9970
3·123	1·489	·9648	4·416	2·106	·9971
3·2	1·5261	·9691	4·5	2·147	·9976
3·22	1·5356	·9701	4·567	2·178	·9979
3·3	1·5738	·9741	4·6	2·1937	·9981
3·336	1·592	·9756	4·7	2·242	·9985
3·4	1·6215	·9781	4·8	2·289	·9988
3·45	1·6453	·9800	4·9	2·3368	·9990
3·5	1·6691	·9817	5·0	2·3845	·9993
3·54	1·689	·9831	5·1	2·432	·9994
3·6	1·7168	·9848	5·2	2·4798	·9995
3·7	1·7645	·9874	5·3	2·5276	·9996
3·729	1·778	·9881	5·4	2·5753	·9997
3·8	1·8122	·9896	5·5	2·6229	·9998
3·89	1·83	·9903	5·6	2·6706	·9998
3·9	1·8599	·9915	5·7	2·7183	·9999
3·913	1·866	·9917	5·8	2·7660	·9999
4·0	1·9076	·9930	5·9	2·814	·99993

TABLE II.

Vapour Pressure of Water.

Rounded off from the values of Scheel and Heuse (*Ann. d. Phys.* 715-736, *31*, 1910).

Temp.	Vap. Press.	Temp.	Vap. Press.
4°	6·1 mm.	19°	16·5 mm.
5°	6·5 ,,	20°	17·5 ,,
6°	7·0 ,,	21°	18·7 ,,
7°	7·5 ,,	22°	19·8 ,,
8°	8·0 ,,	23°	21·1 ,,
9°	8·6 ,,	24°	22·4 ,,
10°	9·2 ,,	25°	23·8 ,,
11°	9·8 ,,	26°	25·2 ,,
12°	10·5 ,,	27°	26·7 ,,
13°	11·2 ,,	28°	28·4 ,,
14°	12·0 ,,	29°	30·1 ,,
15°	12·8 ,,	30°	31·8 ,,
16°	13·6 ,,	31°	33·7 ,,
17°	14·5 ,,	32°	35·7 ,,
18°	15·5 ,,	33°	37·7 ,,

TABLE III.

Boiling Points of Water at various pressures.

Rounded off from the values of Wiebe. Wiebe gives 3 decimal places.

	0	1	2	3	4
740	99·26	99·29	99·33	99·37	99·41
50	99·63	99·67	99·70	99·74	99·78
60	100·00	100·04	100·07	100·11	100·15
	5	6	7	8	9
740	99·44	99·48	99·52	99·56	99·59
50	99·82	99·85	99·89	99·93	99·96
60	100·18	100·22	100·26	100·29	100·33

TABLE IV.

Density of Water.

The last digits were obtained by rounding off from the data of Thiesen, Scheel and Diesselhorst (1900), and of Thiesen (1904).

Temperature.	Density.	Temperature.	Density.
0°	0·99987	21°	0·99802
1°	0·99993	22°	0·99779
2°	0·99997	23°	0·99756
3°	0·99999	24°	0·99732
4°	1·00000	25°	0·99707
5°	0·99999	26°	0·99681
6°	0·99996	27°	0·99654
7°	0·99993	28°	0·99626
8°	0·99988	29°	0·99597
9°	0·99981	30°	0·99567
10°	0·99973	31°	0·99537
11°	0·99963	32°	0·99505
12°	0·99953	33°	0·99473
13°	0·99940	34°	0·99440
14°	0·99927	35°	0·99406
15°	0·99913	40°	0·99224
16°	0·99897	50°	0·98807
17°	0·99880	60°	0·98324
18°	0·99862	70°	0·97781
19°	0·99843	80°	0·97183
20°	0·99823	90°	0·96534

TABLE V.

Viscosity and Surface Tension of Water.

Viscosity (Hosking, 1909).

Viscosity	0·01142	0·01006	0·008926	0·00800
Temp.	15°	20°	25°	30°
Viscosity	0·00724	0·00657	0·00600	0·005500
Temp.	35°	40°	45°	50°

Surface Tension (in moist air).

Surface Tension	74·05	73·26	72·53	71·78	Volkmann.
Temp.	10°	15°	20°	25°	
Surface Tension	71·03		70·29	69·54	Volkmann.
Temp.	30°		35°	40°	
Surface Tension	68·6			67·8	Brunner.
Temp.	45°			50°	

TABLE VI.

Data for Benzene.

Vapour Pressure.

Vapour Press.	250 mm.	300	350	400	450
Temp. Cent.	47·9°	52·6°	57·0°	61·0°	64·4°
Vapour Press.	500 mm.	551	757·5	1018	
Temp. Cent.	67·4°	70°	80°	90°	

The last 3 figures are from Smith and Menzies (*Jour. Am. Chem. Soc.*, 1453, *32*, 1910) and the others are from Kahlbaum (*Zeit. ph. Chem.*, 603, *26*, 1898).

Density (Young, 1910).

Density	0·9006	0·8790	0·8576	0·8357	0·8248
Temp. Cent.	0°	20°	40°	60°	70°

Viscosity (Heydweiller, 1896).

Viscosity	0·007038	0·005522	0·004435	0·003177
Temp. Cent.	14·8°	30·8°	46·9°	78·8°

Surface Tension (Renard and Guye, 1907).

Surface Tension	28·83	26·68	23·53	21·70	20·51
Temp. Cent.	11·4°	31·2°	55·1°	68·5°	78·3°

TABLE VII.

Some Eutectic Points below 0° C.

Solution %.	Eutectic Mixture is ice and one of the following.	Eutectic Point.
29·9	$CaCl_2 \cdot 6H_2O$	−54·9°
39·6	$K_2CO_3 \cdot xH_2O$	−36·5
20·6	$MgCl_2 \cdot 12H_2O$	−33·6
22·4	$NaCl \cdot 2H_2O$	−21·2
38·4	$(NH_4)_2SO_4$	−19·05
41·2	NH_4NO_3	−17·35
18·6	NH_4Cl	−15·8
19·8	KCl	−11·1
27·20	$ZnSO_4 \cdot 7H_2O$	− 6·55
19·0	$MgSO_4 \cdot 12H_2O$	− 3·9
5·93	$Na_2CO_3 \cdot 10H_2O$	− 2·10
3·85	$Na_2SO_4 \cdot 10H_2O$	− 1·2

% means grams of anhydrous salt in 100 grams of solution.

To reach the low temperature necessary to obtain these Eutectic Mixtures from the solutions, use as a cooling-bath a mixture of ether and solid carbon dioxide.

TABLE VIII.

Standard temperatures for use in calibration at higher temperatures (A. L. Day, 1912).

	Temperature. Const. vol. N_2 scale.	Uncertainty.	Atmosphere.
M.P. of Cd - -	320·8	±0·1	Air
M.P. of Zn - -	419·3	±0·1	Air
B.P. of S - -	444·5	±0·1	
M.P. of Sb - -	629·8	±0·2	CO
,, Ag - -	960·0	±0·7	CO
,, Au - -	1062·4	±0·8	CO
,, Cu - -	1082·6	±0·8	CO
* ,, Li_2SiO_3 -	1201·0	±1·0	Air
* ,, Ni - -	1452·3	±2·0	H_2 and N_2
* ,, Pd - -	1549·2	±2·0	Air
* ,, Pt - -	1752·0	±5·0	Air

* Crucibles for all M.P.s except those marked * were of graphite.

TABLE IX.

Standard Temperatures.

Transition Points.

$Na_2CrO_4 + 10H_2O$	19·85
$Na_2SO_4 + 10H_2O$	32·38
$Na_2S_2O_3 + 5H_2O$	48·0
$NaBr + 2H_2O$	50·7
$MnCl_2 + 4H_2O$	58·09
$SrCl_2 + 6H_2O$	61·0
$Na_3PO_4 + 12H_2O$	73·4
$Ba(OH)_2 + 8H_2O$	77·9

TABLE X.

Liquids for Heating.

Liquid.	B.P. at 760 mm.	Change of B.P. for 1 mm. change of press.
Methyl formate	31·75	0·034
Carbon disulphide	46·3	0·042
Acetone	56·1	0·030
Chloroform	61·20	0·035
Methyl alcohol	64·70	0·030
Carbon tetrachloride	76·75	0·044
Benzene	80·2	0·043
n-Propyl alcohol	97·20	0·038
Water	100·00	0·0376
Toluene	110·7	0·042
Phenyl chloride	132·00	0·049
m-Xylene	139·2	0·052
Phenyl bromide	156·15	0·053
Phenol	181·5	0·050
Aniline	184·40	0·051
Nitrobenzene	210·85	0·048
Naphthalene	217·7	0·059
α-Bromonaphthalene	279·6	0·065
Phthalic anhydride	284·5	0·068
Anthraquinone	380	0·075
Sulphur	444·5	0·082

TABLE XI.

Conductivity of $KCl\left(\frac{n}{50}\right)$ (Kohlrausch, Holborn and Diesselhorst).

Temp.	κ	Temp.	κ	Temp.	κ
0°	0·001521	13°	0·002142	26°	0·002819
1°	1566	14°	2193	27°	2873
2°	1612	15°	2243	28°	2927
3°	1659	16°	2294	29°	2981
4°	1705	17°	2345	30°	3036
5°	1752	18°	2397	31°	3091
6°	1800	19°	2449	32°	3146
7°	1848	20°	2501	33°	3201
8°	1896	21°	2553	34°	3256
9°	1945	22°	2606	35°	3312
10°	1994	23°	2659	36°	3368
11°	2043	24°	2712		
12°	2093	25°	2765		

TABLE XII.

Ionic Conductivities at 18° (Kohlrausch), at infinite dilution.

α_{18} is the temperature coefficient for relative rise of l when the temperature rises. Thus

$$\Delta l/l = \alpha_{18}(t° - 18°) \quad \text{or} \quad \Delta l = \alpha_{18} l (t° - 18°).$$

	l_C	α_{18}		l_A	α_{18}
H	315	0·0154	Cl	65·5	0·0216
Na	43·5	0·0244	Br	67·0	0·0215
K	64·6	0·0217	I	66·5	0·0213
Ag	54·3	0·0229	OH	174	0·0180
NH_4	64	0·0222	CH_3COO	35	0·0238
$\frac{1}{2}Mg$	45	0·0256	$\frac{1}{2}SO_4$	68	0·0227
$\frac{1}{2}Ca$	51	0·0247	NO_3	61·7	0·0205
$\frac{1}{2}Sr$	51	0·0247	CNS	56·6	0·0221
$\frac{1}{2}Ba$	55	0·0239			
$\frac{1}{2}Cu$	46	—			

TABLE XIII.

Equivalent Conductivity at Infinite Dilution

at 18°	NaCl	108·99		KNO_3	126·50
	$NaNO_3$	105·33		KCNS	121·30
	KCl	130·10		$KClO_3$	119·70
	KBr	132·30		$AgNO_3$	115·80
	KI	131·1			
at 25°	Acetic acid	389		Cinnamic acid	378·5
	Benzoic acid	381			

Degrees of Ionisation of some Electrolytes at 18°.

	$CuSO_4$	$AgNO_3$	$ZnSO_4$	KCl	KBr
0·1*n*	0·38	0·81	0·39	0·86	0·86
1·0*n*	0·21	0·58	0·23	0·76	
	KI	KNO_3	NaCl	HCl	
0·1*n*	0·86	0·83	0·84	0·92	
1·0*n*	0·79	0 63	0·68	0·71	

Dissociation of Water.

Order of the values of $[H'] \times [OH'] \times 10^{14}$ at

18°	25°	50°
0·5	1·0	5·5

Nernst Liquid Resistance

for conductivity work, consists of 121 grams of mannite, 41 grams of boric acid and 0·06 gram KCl in a litre of aqueous solution. $\kappa = 0{\cdot}00097$ at 18° and temperature coefficient is exceedingly small.

TABLE XIV.

Normal Potentials or Electro-Affinities of Elements.

(Potential Commission of the Bunsen Gesellschaft, 1911.)

The values of ${}_0\epsilon_h$ are given. ${}_0\epsilon_h$ is the E.M.F. of a cell of which one half element is the given electrode and the other half element is the normal hydrogen electrode. When the positive pole of this cell is the pole of the given half element, then value of the potential is written positive. The concentrations are molecular normal.

Substance in lower state of oxidation.	Substance in higher state of oxidation.	${}_0\epsilon_h$	Substance in lower state of oxidation.	Substance in higher state of oxidation.	${}_0\epsilon_h$
K	$K^{\cdot}$	−3·2 ?	Fe	$Fe^{\cdot\cdot\cdot}$	−0·04
Na	$Na^{\cdot}$	−2·8 ?	H_2(gas)	$2H^{\cdot}$	±0·00
Mg	$Mg^{\cdot\cdot}$	−1·55	Cu	$Cu^{\cdot\cdot}$	+0·34
Zn	$Zn^{\cdot\cdot}$	−0·76	$2I'$	I_2(solid)	+0·54
Fe	$Fe^{\cdot\cdot}$	−0·43	Ag	$Ag^{\cdot}$	+0·80
Cd	$Cd^{\cdot\cdot}$	−0·40	$2Hg$	$Hg_2^{\cdot\cdot}$	+0·80
Tl	$Tl^{\cdot}$	−0·32	Hg	$Hg^{\cdot\cdot}$	+0·86
Co	$Co^{\cdot\cdot}$	−0·29?	$2Br'$	Br_2(liquid)	+1·08
Ni	$Ni^{\cdot\cdot}$	−0·22?	$2Cl'$	Cl_2(gas)	+1·35
Pb	$Pb^{\cdot\cdot}$	−0·12	Au	$Au^{\cdot}$	+1·5 ?
Sn	$Sn^{\cdot\cdot}$	−0·10	$2F'$	F_2(gas)	+1·9 ?

The degree of uncertainty in Tables XIV. and XV. arises from the uncertainty of obtaining the correct liquid-contact potentials and the correct ion-concentrations and from temperature differences. Only for the calomel electrode is the third decimal place given. Those marked ? are less reliable than the others, on account of uncertainty of measurement or of calculation.

TABLE XV.

Normal Potentials.

Oxidation-Reduction Potentials.

(Potential Commission, Bunsen Gesellschaft, 1911.)

Substances in lower state of oxidation.	Substances in higher state of oxidation.	0^{ϵ}_{h}
$H_2(gas)+2OH'$	$2H_2O$	−0·82
$Pb+SO_4''$	$PbSO_4(solid)$	−0·34
$Cu^{\cdot}$	$Cu^{\cdot\cdot}$	+0·17
$Hg_2Cl_2(solid)+2Cl'$	$2HgCl_2$	+0·24
*$2Hg+2Cl'$	$Hg_2Cl_2(solid)$	+0·275
$4OH'$	$O_2(gas)+2H_2O$	+0·41
$MnO_2(solid)+4OH'$	$MnO_4''+2H_2O$	+0·52
$Fe^{\cdot\cdot}$	$Fe^{\cdot\cdot\cdot}$	+0·75
$Hg_2^{\cdot\cdot}$	$2Hg^{\cdot\cdot}$	+0·92
$2H_2O$	$O_2+4H^{\cdot}$	+1·23
$Cr^{\cdot\cdot\cdot}+4H_2O$	$HCrO_4''+7H^{\cdot}$	+1·3?
$Mn^{\cdot\cdot}+2H_2O$	$MnO_2+4H^{\cdot}$	+1·35
$Pb^{\cdot\cdot}+2H_2O$	$PbO_2+4H^{\cdot}$	+1·44
MnO_2+2H_2O	$MnO_4''+4H^{\cdot}$	+1·63
$PbSO_4(solid)+2H_2O$	$PbO_2(solid)+4H^{\cdot}+SO_4''$	+1·66
$Pb^{\cdot\cdot}$	$Pb^{\cdot\cdot\cdot\cdot}$	+1·8?

* Not the same as 1·0*n*KCl calomel electrode.

In Tables XIV. and XV. raising the concentration of the substances in the lower state of oxidation moves the half-element up the potential list towards the negative end. Raising the concentration of the substances in the higher state of oxidation moves the half-element down the potential list towards the positive end. See formula on page 171.

TABLE XVI.

Useful Data.

Change of Logarithmic Base.

$$2{\cdot}3026 \log_{10} N = \log_e N.$$
$$\log_{10} N = {\cdot}4343 \log_e N.$$

Units of Length.

1 mm. $= 10^{-3}$ metre. 1 cm. $= {\cdot}3937$ inch.
1 micron $= \mu = 10^{-6}$ metre. 2·54 cms. $= 1$ inch.
1 millimicron $= \mu\mu = 10^{-9}$ metre.
1 tenthmetre $= 1$Å.U. $= 10^{-10}$ metre.

Weight.

Avoirdupois: 1 lb. $= 0{\cdot}4536$ kilogram, 1 kilogram $= 2{\cdot}2046$ lbs.
1 oz. $= 28{\cdot}350$ grams, 1 gram $= 0{\cdot}03527$ oz.

Troy: 1 pound $= 0{\cdot}3732$ kilogram, 1 kilogram $= 2{\cdot}7238$ pounds.
1 ounce $= 31{\cdot}1$ grams, 1 gram $= 0{\cdot}0321$ ounce.

Force and Pressure.

In C.G.S. system *force* is measured in *dynes*, and *pressure* in *dynes per cm²*.

1 *atmosphere* $= 1{\cdot}0132 \times 10^6$ dynes per cm².
$\equiv 760$ mm. of Hg at 0° C. and 45° lat. at sea level.
1 *megabar* $= 10^6$ dynes per cm².
$\equiv 750$ mm. of Hg at 0° C. and 45° lat. at sea level.

Energy.

In C.G.S. Units.	In Electrical Units.	In Heat Units.
1 *erg*	$= 10^{-7}$ *watt-seconds* or *joules*	$= {\cdot}239 \times 10^{-7}$ *small calories.*
10^7 *ergs*	$= 1$ *watt-second* or *joule*	$= {\cdot}239$ *small calories.*
$4{\cdot}18 \times 10^7$ *ergs*	$= 4{\cdot}18$ *watt-seconds* or *joules*	$= 1$ *small calorie.*

Energy-rate or Power.

1 *watt* = 1 *volt-ampère.*
746 *watts* = 1 *horse-power* = 1 H.P.
1 *kilowatt* = 1·34 H.P.
Power × time = energy,

thus: *watt-seconds* = *volt-ampère-seconds* = *volt-coulombs* = *joules.*
1 *kilowatt-hour* = 1000 × 3600 *watt-seconds*
$= 3{\cdot}6 \times 10^6$ *watt-seconds* = 1 *Board of Trade Unit.*

R, **the Gas Constant** for 1 gram mol., has the following values: according as energy is measured in ergs, joules or calories, the value of R is $8{\cdot}315 \times 10^7$, 8·315 or 1·988.

Absolute Temperature.

$T = t + 273{\cdot}09$, where T = temp. abs. and t = temp. C.;
or $T = t + 273{\cdot}1$ (approximately).

"Liquid" Platinum.

Moisten 0·3 gram of platinic chloride with conc. HCl and mix with 1 c.c. of conc. boric acid solution. Dissolve in alcohol and add 1 c.c. of French turpentine and 2 c.c. of oil of lavender.

Density of Alcohol.

Pure Alcohol (Young, 1910).

Density	0·7979	0·7894	0·7810	0·7722	0·7633
Temp.	10°	20°	30°	40°	50°

Aqueous Solutions of Alcohol (Osborne and M'Kelvy, 1911).

Density (15°/4°)	0·7936	0·79666	0·79971	0·80269	0·80564
Weight of alcohol in 100 grams of solution	100	99	98	97	96

Density of Acetone.

Density (15°/4°) 0·7971
Coeff. of cubic expansion at 20° = 0·001487

International Atomic Weights. 1914.

Element.	Symbol.	Atomic Weight.	Uncertainty.
Aluminium	Al	27·1	±0·1
Antimony	Sb	120·2	±0·3
Argon	A	39·88	±0·02
Arsenic	As	74·96	±0·05
Barium	Ba	137·37	±0·03
Beryllium*	Be	9·1	±0·05
Bismuth	Bi	208·0	±0·1
Boron	B	11·0	±0·05
Bromine	Br	79·92	±0·02
Cadmium	Cd	112·40	±0·03
Caesium	Cs	132·81	±0·05
Calcium	Ca	40·07	±0·03
Carbon	C	12·00	±0·005
Cerium	Ce	140·25	±0·1
Chlorine	Cl	35·46	±0·01
Chromium	Cr	52·0	±0·05
Cobalt	Co	58·97	±0·02
Copper	Cu	63·57	±0·05
Dysprosium	Dy	162·5	±0·2
Erbium	Er	167·7	±0·2
Europium	Eu	152·0	±0·2
Fluorine	F	19·0	±0·05
Gadolinium	Gd	157·3	±0·2
Gallium	Ga	69·9	±0·5
Germanium	Ge	72·5	±0·5
Gold	Au	197·2	±0·1
Helium	He	3·99	±0·01
Holmium	Ho	163·5	±0·1
Hydrogen	H	1·008	±0·0005
Indium	In	114·8	±0·2
Iodine	I	126·92	±0·03
Iridium	Ir	193·1	±0·2
Iron	Fe	55·84	±0·03
Krypton	Kr	82·92	±0·1
Lanthanum	La	139·0	±0·3
Lead	Pb	207·10	±0·1
Lithium	Li	6·94	±0·05
Lutecium	Lu	174·0	±0·5
Magnesium	Mg	24·32	±0·03
Manganese	Mn	54·93	±0·05
Mercury	Hg	200·6	±0·4
Molybdenum	Mo	96·0	±0·1

* Beryllium = Glucinum = Gl.

International Atomic Weights. 1914.—(*Continued.*)

Element.	Symbol.	Atomic Weight.	Uncertainty.
Neodymium	Nd	144·3	±0·5
Neon	Ne	20·2	±0·02
Nickel	Ni	58·68	±0·02
Niobium*	Nb	93·5	±0·2
Niton	Nt	222·4	±0·3
Nitrogen	N	14·01	±0·005
Osmium	Os	190·9	±0·4
Oxygen	O	16·00	basis
Palladium	Pd	106·7	±0·1
Phosphorus	P	31·04	±0·1
Platinum	Pt	195·2	±0·1
Potassium	K	39·10	±0·01
Praseodymium	Pr	140·6	±0·5
Radium	Ra	226·4	±0·3
Rhodium	Rh	102·9	±0·05
Rubidium	Rb	85·45	±0·05
Ruthenium	Ru	101·7	±0·1
Samarium	Sa	150·4	±0·2
Scandium	Sc	44·1	±0·2
Selenium	Se	79·2	±0·1
Silicon	Si	28·3	±0·1
Silver	Ag	107·88	±0·02
Sodium	Na	23·00	±0·01
Strontium	Sr	87·63	±0·03
Sulphur	S	32·07	±0·01
Tantalum	Ta	181·5	±1·0
Tellurium	Te	127·5	±0·2
Terbium	Tb	159·2	±0·5
Thallium	Tl	204·0	±0·2
Thorium	Th	232·4	±0·5
Thulium	Tm	168·5	±1·0
Tin	Sn	119·0	±0·5
Titanium	Ti	48·1	±0·1
Tungsten	W	184·0	±0·5
Uranium	U	238·5	±0·5
Vanadium	V	51·0	±0·1
Xenon	Xe	130·2	±0·2
Ytterbium (Neoytterbium)	Yb	172·0	±1·0
Yttrium	Y	89·0	±0·2
Zinc	Zn	65·37	±0·05
Zirconium	Zr	90·6	±0·2

* Niobium = Columbium = Cb.

	0	1	2	3	4	5	6	7	8	9	1 2 3	4 5 6	7 8 9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4 9 13 4 8 12	17 21 26 16 20 24	30 34 38 28 32 36
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4 8 12 4 7 11	15 19 23 15 19 22	27 31 35 26 30 33
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3 7 11 3 7 10	14 18 21 14 17 20	25 28 32 24 27 31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3 7 10 3 7 10	13 16 20 13 16 19	23 26 30 22 25 29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3 6 9 3 6 9	12 15 19 12 15 17	22 25 28 20 23 26
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3 6 9 3 6 8	11 14 17 11 14 17	20 23 26 19 22 25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3 5 8 3 5 8	11 14 16 10 13 16	19 22 24 18 21 23
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	3 5 8 2 5 7	10 13 15 10 12 15	18 20 23 17 20 22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2 5 7 2 5 7	9 12 14 9 11 14	16 19 21 16 18 21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2 4 7 2 4 6	9 11 13 8 11 13	16 18 20 15 17 19
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2 4 6	8 11 13	15 17 19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2 4 6	8 10 12	14 16 18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2 4 6	8 10 12	14 15 17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2 4 6	7 9 11	13 15 17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2 4 5	7 9 11	12 14 16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2 3 5	7 9 10	12 14 15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2 3 5	7 8 10	11 13 15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2 3 5	6 8 9	11 13 14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2 3 5	6 8 9	11 12 14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1 3 4	6 7 9	10 12 13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1 3 4	6 7 9	10 11 13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1 3 4	6 7 8	10 11 12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1 3 4	5 7 8	9 11 12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1 3 4	5 6 8	9 10 12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1 3 4	5 6 8	9 10 11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1 2 4	5 6 7	9 10 11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1 2 4	5 6 7	8 10 11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1 2 3	5 6 7	8 9 10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1 2 3	5 6 7	8 9 10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1 2 3	4 5 7	8 9 10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1 2 3	4 5 6	8 9 10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1 2 3	4 5 6	7 8 9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1 2 3	4 5 6	7 8 9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1 2 3	4 5 6	7 8 9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1 2 3	4 5 6	7 8 9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1 2 3	4 5 6	7 8 9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1 2 3	4 5 6	7 7 8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1 2 3	4 5 5	6 7 8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1 2 3	4 4 5	6 7 8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1 2 3	4 4 5	6 7 8

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

	0	1	2	3	4	5	6	7	8	9	1 2 3	4 5 6	7 8 9
·00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0 0 1	1 1 1	2 2 2
·01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0 0 1	1 1 1	2 2 2
·02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0 0 1	1 1 1	2 2 2
·03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0 0 1	1 1 1	2 2 2
·04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0 1 1	1 1 2	2 2 2
·05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0 1 1	1 1 2	2 2 2
·06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0 1 1	1 1 2	2 2 2
·07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0 1 1	1 1 2	2 2 2
·08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0 1 1	1 1 2	2 2 3
·09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0 1 1	1 1 2	2 2 3
·10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0 1 1	1 1 2	2 2 3
·11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0 1 1	1 2 2	2 2 3
·12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0 1 1	1 2 2	2 2 3
·13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0 1 1	1 2 2	2 3 3
·14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0 1 1	1 2 2	2 3 3
·15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0 1 1	1 2 2	2 3 3
·16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0 1 1	1 2 2	2 3 3
·17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0 1 1	1 2 2	2 3 3
·18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0 1 1	1 2 2	2 3 3
·19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0 1 1	1 2 2	3 3 3
·20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0 1 1	1 2 2	3 3 3
·21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0 1 1	2 2 2	3 3 3
·22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0 1 1	2 2 2	3 3 3
·23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0 1 1	2 2 2	3 3 4
·24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0 1 1	2 2 2	3 3 4
·25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0 1 1	2 2 2	3 3 4
·26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0 1 1	2 2 3	3 3 4
·27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0 1 1	2 2 3	3 3 4
·28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0 1 1	2 2 3	3 4 4
·29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0 1 1	2 2 3	3 4 4
·30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0 1 1	2 2 3	3 4 4
·31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0 1 1	2 2 3	3 4 4
·32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0 1 1	2 2 3	3 4 4
·33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0 1 1	2 2 3	3 4 4
·34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1 1 2	2 3 3	4 4 5
·35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1 1 2	2 3 3	4 4 5
·36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1 1 2	2 3 3	4 4 5
·37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1 1 2	2 3 3	4 4 5
·38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1 1 2	2 3 3	4 4 5
·39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1 1 2	2 3 3	4 5 5
·40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1 1 2	2 3 4	4 5 5
·41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1 1 2	2 3 4	4 5 5
·42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1 1 2	2 3 4	4 5 6
·43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1 1 2	3 3 4	4 5 6
·44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1 1 2	3 3 4	4 5 6
·45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1 1 2	3 3 4	5 5 6
·46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1 1 2	3 3 4	5 5 6
·47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1 1 2	3 3 4	5 5 6
·48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1 1 2	3 4 4	5 6 6
·49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1 1 2	3 4 4	5 6 6

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
·50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
·51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
·52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
·53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
·54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
·55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
·56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
·57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
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·60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
·61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
·62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
·63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
·64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
·65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
·66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
·67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
·68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
·69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
·70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
·71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
·72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
·73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
·74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
·75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
·76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
·77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
·78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
·79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
·80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
·81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
·82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
·83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
·84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
·85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
·86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
·87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
·88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
·89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
·90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
·91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
·92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
·93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
·94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
·95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
·96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
·97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
·98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
·99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20

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